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1975 ERC/RTP Review

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Research Triangle Park, North Carolina 27711

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16. ABSTRACT

This report is a review and evaluation of the current knowledge of the criteria and hazardous pollutants: oxides of nitrogen; carbon monoxide; hydrocarbons; photochemical oxidants; suspended particulates; sulfur oxides; asbestos; beryllium; and mercury. Primary emphasis is on results achieved from the ERC/RTP research program since publication of the criteria documents, which were used as the data bases for the National Ambient Air Quality Standards. This document is the first in a series of annual reviews to be conducted by the Environmental Research Center in the Research Triangle Park, N.C. on the results of on-going research.

The document attempts to assess the adverse effects of the criteria and hazardous pollutants on health, vegetation, climate, visibility, and materials. Information on instrumentation, measurement, pollutant characterization, transformation and transport, and control technology for the specific pollutants is also given.

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Chemical Analysis	Hydrocarbons	Air Pollution	06A	07C
Abatement	Photochem. Oxidants		13B	07D
Distribution	Particulates		04B	07D
Environ. Biology	Sulfur Oxides		06B	07B
Oxides of Nitrogen	Asbestos		07B	07B
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U.S. ENVIRONMENTAL PROTECTION AGENCY
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PREFACE

This report was prepared by Environmental Research Center, Research Triangle Park (ERC/RTP) staff. The report's objective is to review results of research by and under the sponsorship of ERC/RTP, related to criteria and hazardous pollutants since publication of the criteria and background documents. Recent reviews are also included in a series of documents by the Committee on Challenges to Modern Society, NATO; and by the National Academy of Science.

This report does not duplicate those other reviews. Primary emphasis here is on results of the ERC/RTP research program. Significant results of still other investigators known to the authors, however, are included. But it is not a complete review and evaluation of all current literature.

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1. SUMMARY

1.1 GENERAL DISCUSSION

The best scientific data base was unavailable for six air pollutants when National Ambient Air Quality Standards (NAAQS) were set. This data base is still inadequate. However, evidence gathered since the NAAQS were set support the standards.

A recent in-depth review by the National Academy of Sciences (NAS)* indicated that there was no good reason relative to health and welfare effects to change the standards. In some cases, for example, safety factors were minimal compared to those factors used to control pollutants such as radiation.

The National Academy of Sciences' report comprehensively reviews the scientific data base for NAAQS. The details of material included in the NAS reports will not be duplicated here. Summary material will be included, however, when appropriate for completeness.

In this review, primary emphasis is on results achieved from the ERC/RTP research and development program since publication of criteria and background documents.

Air pollutants include complex combinations of reactive sulfur, nitrogen, inorganic and organic compounds from man-made and natural sources. Man and other species and materials are exposed to varying amounts of this mixture of pollutants at different times. The biological response to exposure is different for different species and pollution combinations. Physical properties of the environment such as temperature and humidity may also influence the response.

---

*Air Quality and Automobile Emissions Control, A Report by the Coordinating Committee on Air Quality Studies, National Academy of Sciences, National Academy of Engineering (4 Volumes), dated September 1, 1974. Prepared for the Committee on Public Works, U.S. Senate.

Parts of this review consider things such as atmospheric transport, certain analytical techniques and control technology common to each classification of pollutants. Material on specific pollutants is also presented with awareness that such pollutants contribute to the total pollution burden in the atmosphere. A brief general discussion is included in each section of the report.

1.2 INSTRUMENTATION

Since NAAQS were set, significant progress has been made in development of sampling, analytical and instrumental methods to measure ambient and source concentrations of air pollutants--particularly in areas of chromatography, spectroscopy and chemiluminescence. Programs in method calibration, interlaboratory comparison, quality assurance and station siting have been developed and are being implemented. Although the over-all monitoring program is still inadequate, the above efforts have added much to the quality of aerometric data.

1.2.1 Nitrogen Oxides

An improved 24-hour wet chemical method of sampling and analysis (TGS method) for ambient NO_2, and an instrumental method (Chemiluminescent) for NO, NO_2, NO_x, has been developed over the past three years. The chemiluminescent method is now widely used for continuous monitoring of ambient oxides of nitrogen along with the TGS and other methods and is being considered as a replacement for the current Federal Reference method.

Guidelines have been proposed for selection and use of continuous monitoring systems for NO_x emissions from chosen stationary sources.

The criteria and procedures for determining acceptability of a candidate ambient air-monitoring method, equivalent to the prescribed reference method, have been proposed.

Chemiluminescence is widely accepted as the most selective, accurate and rapid means of NO_x analysis of mobile source emissions.

1.2.2 Carbon Monoxide

Automated gas-chromatography instruments capable of semi-continuously monitoring ambient air CO concentrations over a range of 0.1 to 1000 ppm are now commercially available. Improvements in methods for generation of known concentrations of CO are under development.

The EPA reference method for measurement of CO from stationary sources (continuous sampling coupled with a Non-Dispersive Infrared analysis) is considered the most reliable of available methods. Primary problems involve particulates, water vapor and CO_2. But recent advances in NDIR technology have minimized these problems.

Gas correlation spectroscopy has been developed as an improved method to measure CO emissions from mobile sources. The technique can measure the expected low concentrations from light-duty vehicles of FY 1976 and later.

1.2.3 Hydrocarbons

A commercial non-methane reactive hydrocarbon analyzer is now available. The system converts all hydrocarbons except methane to H_2O and CO_2--the methane is continuously monitored with a flame ionization detector (FID) and total hydrocarbons are monitored with a second detector. A chemiluminescent method to monitor reactive hydrocarbons and olefinic organics (such as ethylene and vinyl chloride) has been partially developed. EPA has not yet required the states to monitor hydrocarbons in support of the State Instrumentation Plans (SIP).

Emission standards for hydrocarbons from stationary sources have not been set. No measurements are therefore required. Both total hydrocarbons and non-methane hydrocarbon instrumentation developed for ambient air measurements have been used to measure emissions from stationary sources. These systems do not settle the question of their applicability to emission standard settings. The present research and development effort involves grab-sampling systems for class fractions that are then analyzed in the laboratory using chromatographic methods. The analytical methods for polynuclear aromatics are not completely satisfactory. The procedures are complicated and reproducibility and sensitivity are problems.

Current Federal regulations of total hydrocarbon emissions from mobile sources utilize flame ionization analysis. Techniques have been developed to measure detailed composition, total non-reactive hydrocarbons and methane. Work is in progress to develop methods to measure other reactive components such as osygenates.

1.2.4 Photochemical Oxidants

The Federal Reference method for ozone measurements in ambient air is based on the chemiluminescent reaction of O_3 with ethylene. A number of chemiluminescent methods are now available commercially. These ozone monitors are calibrated with ozone generators whose output has been determined using the neutral buffered KI method. The calibration procedure is not completely satisfactory, but work is underway to improve the procedure.

1.2.5 Particulate Matter

New procedures to collect aerosols in the fine and coarse particle size-ranges are in final stages of development and will be tested in CY 1975. With these collection procedures, sample deposit profiles are well suited for rapid mass analysis by the beta gauge for mass and by x-ray flourescence for elements with atomic numbers above 12.

Methods to determine the rate of particulate matter emissions, mass concentrations, visible emission (opacity) selection of sampling ports, stack gas velocity, stack gas molecular weight and stack gas moisture from certain types of stationary sources have been published. To date, most measurements methods have been concerned with mass emissions and valid sampling techniques. Work is underway to develop satisfactory methods to determine size distribution using inertial and optical techniques.

Methods to determine the composition of particulates emitted from stationary sources are being studied. The most attractive method currently for routine multielemental analysis of particulate matter from stationary sources is x-ray fluorescence (XRF) spectroscopy. A wavelength dispersion multispectrometer instrument, recently set up at ERC/RTP, permits rapid analysis of all elements higher than oxygen in atomic number with the high degree of spectral resolution needed for airborne particulate samples.

Particulate measurement techniques have been developed for light-duty mobile sources using a dilution technique. Measurements are currently made gravimetrically. Instruments to do that measuring are being developed.

1.2.6 Sulfur Oxides

Several major improvements in methods to measure ambient air concentrations of sulfur dioxide and sulfate have been developed over the past three years. Sensitivity, specificity and stability of field monitoring systems for SO_2 offered commercially during the 1970's have been greatly improved over those available in the 1960's. Improved methods to measure sulfate and sulfuric acid in ambient air are being developed.

Specifications for SO_2-continuous-monitoring systems for stationary sources and ambient air have been published or proposed.

Sulfuric acid emissions from vehicles with exhaust oxidation catalyst systems for CO and hydrocarbon control have stimulated work to develop measurement techniques for sulfur in fuel and for sulfur oxides, sulfuric acid and sulfates in exhaust emissions. Techniques have been developed and are in use. Work is in progress to develop real-time methods.

1.2.7 Asbestos

The present National Emissions Standards for Hazardous Pollutant (NESHAP) regulation for asbestos emissions is based upon prescribed control practices. The most common measurement technique involves electron microscopy to identify, count and size fibers. Development of a new and more rapid measurement method is under way using the x-ray diffraction technique on a sample pretreated for fiber alignment.

1.2.8 Beryllium

A measurement method for beryllium emissions involving isokinetically sampling with a particulate sampling train and analyzing the sample by atomic absorption technique is described in the Federal Register. A continuous monitoring technique is not available as a proven method applicable to emission sources.

1.2.9 Mercury

The measurement method for mercury prescribed in the Federal Register involves isokinetically sampling emissions in a solution of iodine monochloride with analysis by spectrophotometry. A continuous monitoring system can be developed through use of available analytical systems in conjunction with an appropriate automated sampling interface system. Development of such an interface system is under way.

1.2.10 Methods Standardization and Performance Evaluation

EPA is standardizing reference methods for individual air pollutants in ambient air and stationary and mobile sources. The program includes in-house methods evaluation and ruggedness testing, method inter-relatability studies and collaborative testing. All criteria pollutants are under study and some results have been published for all six criteria pollutants.

1.3 ENVIRONMENTAL APPRAISAL

Essentially all man-made atmospheric matter classified as pollutants are also produced by natural sources. Emissions produced by man-made sources are superimposed on the "natural background." Trace gases are naturally emitted from geophysical and biological sources. Natural sources produce a major portion of particulate matter found in the atmosphere. Crude models for sulfur and nitrogen cycles are available, but they are not sufficiently accurate to determine the contribution of air pollutants from man-made activities to atmospheric loading. At present, only limited attention is given to problems relating to natural sources and removal mechanisms that impact on global or regional balances of air pollutants.

Limited data are available on emissions from selected classes of stationary and mobile sources. They only permit crude estimates of the contribution to atmospheric loading. An effort is under way to get improved emission factors for both stationary and mobile sources.

1.3.1 Emissions

1.3.1.1 Oxides of Nitrogen Emissions--It is estimated that stationary sources contribute at least half of the NO_x emissions of man-made sources in the U.S. The 1972 estimate was over eleven-million tons. About 98% of total emissions were produced by combustion of fossil fuels. The remainder was from industrial processes such as manufacture of nitric acid, sulfuric acid and explosives.

Nationwide, mobile sources contribute about 50% of the total man-made emissions of NO_x. In some urban areas such as Los Angeles, however, the percentage is much higher. Oxides of nitrogen are formed in mobile sources primarily by the fixation of atmospheric nitrogen in the combustion process. Exhaust gas recirculation (EGR) and water injection schemes reduce the peak temperature attained and this reduces the NO_x emissions. Use of these methods on light-duty vehicles have reduced NO_x emissions significantly (50% between 1968 and 1973 models).

1.3.1.2 Carbon Monoxide Emissions--Preliminary results of tests on 1975 prototype light-duty vehicles equipped with oxidation catalyst-converters indicate that these vehicles will meet the 1975 standard of 15 gm/mi. In some cases, the results were better than the 1976 standard of 3.4 gm/mi. Reported values of CO emissions from the only commercially available car equipped with the stratified charge engine (Honda CVCC) was 2 gm/mi.

1.3.1.3 Hydrocarbon Emissions--The Clean Air Act requires a 90% rollback from the 1970 levels of hydrocarbon emissions from light-duty vehicles. The standard for 1976 models will be 0.41 gm/mi. Preliminary tests indicate that this standard is being achieved in prototype vehicles. Tests indicate that the relative percentage of methane in emissions from vehicles equipped with catalytic controls is increased--approximately 80% of the hydrocarbon emissions with catalytic controls may be methane. Ford Company has asked that emission standards be changed to exempt methane. This proposal is currently under review.

1.3.1.4 Sulfur Oxides Emissions--Trace qualities of sulfur primarily in the form of organic sulfur compounds are present in gasoline. During normal combustion processes, this sulfur is converted to SO_2 and SO_3 (about 98% SO_2). The SO_3 reacts rapidly with water in the exhaust and is emitted as sulfuric acid or sulfate particulate. The amount of SO_2 and SO_3 emitted from mobile sources is negligible (less than 1%) compared to that of stationary sources. Light-duty vehicles equipped with catalytic convertors emit higher concentrations of sulfuric acid and sulfates than those vehicles without these devices. This may result in significant concentrations of sulfur oxide emissions in high traffic density areas.

1.3.2 Ambient Concentrations

Because of uncertainties in emission and air quality data, it is difficult to establish a quantitative relationship between trends.

However, some qualitative estimates can be made. Since the national ambient air quality standards were set and control strategies implemented, air quality data indicates a downward trend in CO and particulate matter pollutants. Oxides of nitrogen concentrations have increased, but urban concentrations have decreased. No significant change in sulfate concentrations is evident despite reduction in urban SO_2 levels. There is some evidence that non-urban sulfate concentrations may have increased.

Ambient CO trends should directly reflect exhaust emissions from motor vehicles. Since introduction of CO emissions controls, the average CO emission rate has decreased. The annual average CO concentration for selected urban areas appears to have decreased. Instrumentation problems and operating procedures have biased the data in some areas.

The annual average concentration of nitric oxide (NO) has increased. The pattern is less consistent for NO_2 and total oxides of nitrogen. This increase is attributed to increase in fuel combustion and introduction of control systems for CO and hydrocarbons on mobile sources that in some cases produced increased emissions of nitrogen oxides.

Trends for photochemical oxidants are not well established. The data in general suggest a decrease in urban concentrations. However, there is now much evidence that ozone concentration in certain non-urban regions is increasing (Northeast U.S.).

There are few data available on ambient concentrations of mercury, asbestos and beryllium.

1.4 TRANSFORMATION AND TRANSPORT

The relationship between emissions and atmospheric loading or air quality is dependent on transformation, transport and removal processes in the ambient atmosphere. These processes are greatly affected by meteorology and terrain. The extent that these processes contribute to chemical characteristics and temporal and spatial distribution of criteria and hazardous pollutants is often not well known.

Once pollutants are emitted into the atmosphere, they are subject to various chemical reactions. A polluted atmosphere is a very dynamic mixture of reactive gases and aerosols. It is this mixture that man and materials are exposed to.

Although the photochemistry of nitrogen oxides has been widely studied, only about 50% of the nitrogen emitted into the atmosphere has been accounted for. Recent investigation suggests that nitric acid is produced in the atmosphere by photolytic processes. Nitrous acid is not formed in as great a quantity as nitric acid, but is important in photochemical smog production because of the highly reactive radicals produced. Many questions remain to be answered about quantitative relationship between NO_x, oxidant and hydrocarbons in urban and non-urban atmosphere.

New findings on pollutant transport and conditions of hydrocarbon oxidation have led to a new reactivity classification for organic compounds. Under the prolonged irradiation conditions of transported air masses, organic compounds formerly classified as "less reactive" can yield as much oxidant as some classified "more reactive." Recent smog chamber experiments have produced quantitative oxidant-HC-NO_x relationships. The applicability of these findings to the real atmosphere, however, remains questionable. These results suggest coordinated control of HC and NO_x as the most effective means of oxidant reduction.

Major advances have been made in understanding the sources, properties, chemical composition and dynamics of atmospheric aerosols. Effective control techniques must consider particle size and particle composition as well as precursors (SO_2, NO_x and certain organics). Research work has identified a multimodal distribution of the atmospheric aerosol.

Secondary sulfate, nitrate and organic aerosols comprise the major part of fine particulate (one mode) matter. Road dust, tire debris and other materials generated by vehicular traffic are a major source of coarse particles in urban areas. Organic material is a major primary and secondary component of fine particulate matter.

The transformation that converts SO_2 to sulfate is better understood and measurements of transformation rates in power plant plumes and urban atmosphere have been made. Progress has been made in chemical characterization of atmospheric aerosols and further work is under way.

A solution to regional sulfate pollution problems will require an understanding of how sulfates are formed in the atmosphere. Chemical mechanisms for the transformation are not well known. Chemical oxidation by photochemically generated intermediates and catalytic oxidation are currently being emphasized as the most likely mechanisms. Both laboratory and field studies are under way.

No significant oxidation reaction of CO has been found for urban air.

Models have been developed to estimate pollutant concentrations over an urban area. A User's Network for Applied Modeling of Air Pollution (UNAMAP) was put into operation in May 1973. This program gives interested agencies current air-quality simulation models via a teletype-processing network. A fluid modeling facility is being established to study the flow and diffusing of pollutants around buildings, highway configurations and complex terrain. A regional air pollution study is now under way in St. Louis, Missouri that provides data for validation and improvement of pollution simulation models.

1.5 EFFECTS

National ambient air quality standards were established in reference to an incomplete data base. The standards were designed, based upon available information, to include a margin of safety sufficient to protect the health of the most sensitive segments of our society. Since setting the standards, a continuing research effort has provided additional effects information. Although the data base is still inadequate, recent reviews by the National Academy of Sciences (NAS) and the National Institute for Environmental Health Sciences (NIEHS) have concluded that the standards should not be changed at this time. However, the NAS suggested that consideration be given to establishment of an hourly standard for NO_2.

Recent evidence suggests that secondary aerosols or combinations of aerosols and gases are better correlated with adverse health effects than are gaseous pollutants. The size distribution and chemical composition of the aerosols appear to significantly influence the biological response.

1.5.1 Human and Animal

1.5.1.1 Nitrogen Dioxide and Suspended Nitrates--The limited number of studies on human health effects of NO_2 reveal many gaps in the information base for the primary national standard. The few studies that have been conducted are confounded by the presence of high levels of other pollutants that have not been appropriately disentangled. Measurement data used in these studies was also limited either by use of too few sampling stations or use of an unreliable measurement method for NO_2 or both.

A continuous monitoring instrument using the chemiluminescence reaction between ozone and nitrogen oxide is considered more reliable than either the Jacobs Hochheiser or the Saltzman method for measuring nitrogen dioxide (that can be reproducibly converted to nitric oxide). The chemiluminescent reaction is currently being used in new health studies but information from such studies is not yet available.

In the Chattanooga study (on which the NO_2 standard was based), the high NO_2 levels also were accompanied by relatively high levels of suspended nitrates. The recent linking of asthma attacks to suspended nitrates raises the question as to whether or not suspended nitrates may have contributed to the observed adverse health effects in the Chattanooga study. The observed human effects support reasonably well the biological effects observed in experimental animal studies using NO_2 as a single pollutant.

However, it has been reported that in some NO_2 rich atmospheres of animal exposure chambers, ammonum nitrate may be generated in fairly large quantities. This suggests that in some instances suspended nitrates as well as NO_2 may have been contributing to atmospheric exposure in animal studies. In any study involving exposure of animals to NO_2, the extent of reduction of NO_2 must be considered.

Five categories of human health effects have been identified in association with NO_2; acute toxic, often fatal reactions; diminished lung function; structural and biochemical changes in lungs that are most likely to promote development of chronic respiratory disease; susceptibility to infection; and systemic effects.

There is enough information from both human and animal studies to determine the levels of NO_2 that may contribute to toxic reactions. However, there are very few points on the lower part of the dose-response curve to provide information on the levels of NO_2 that may contribute to susceptibility to infection and development of chronic respiratory disease. Further human studies are necessary that address the contribution of NO_2 and its degradation products to insidious chronic disease. Until such information is available, it seems appropriate to maintain the present standard. It provides a reasonable margin of safety based on both animal and human studies to date.

In the New York-New Jersey metropolitan area, a study of 373 asthmatics followed daily for eight months showed that increased asthmatic attacks were significantly associated with ambient suspended nitrates. The observed increased risk of asthmatic attacks related to increased concentrations of nitrates occurred only at a temperature of 10° centigrade or above. In another study in two southeast communities there was evidence of excess risk of asthmatic attacks with elevated levels of suspended nitrates at higher temperatures. But the findings were less consistent than those observed in the New York-New Jersey area.

Preliminary findings of a study of 512 asthmatics in seven communities in the Los Angeles Basin also show significant association of asthmatic attacks with suspended nitrates. But the full data analyses of this study has not yet been completed. Nitrogen dioxide was not significantly associated with asthma attack rates in any of these studies.

Very little is known about inhalation toxiciology of inorganic nitrates. If the associations between airborne nitrates and asthmatic attacks are causal, airborne nitrates may be an important respiratory irritant.

Pathologic effects of NO_2 on the respiratory tract have been induced in experimental animals at concentrations at and above 2 PPM. Exposure to concentrations of 10-25 ppm on a continuous basis has produced pulmonary emphysema-like disease in rats, mice, dogs, and rabbits. The biological response appears to be different when the experimental animal is exposed to oxidant and NO_2, although the results are not yet conclusive.

The NO_2 effect was obscured when equal parts of NO_2 and O_3 were used. The physical appearance of emphysema varied with the species studied and was possibly influenced by differences in the size and frequency of inter-alveolar pores.

The biochemical mechanisms by which NO_2 reacts with tissue resembles O_3 to some degree because of their common oxidizing properties. A biochemical study is being done to examine the prospect that toxicity of NO_2 and O_3 may be an "ultimate" toxicant produced by a reaction between the oxidant and unsaturated fatty acid. Ozone is known to react with unsaturated fatty acids to produce fatty acid ozonides. NO_2 similarly can react with unsaturated fatty acids to produce nitroxide fatty acids that are likely to be very reactive.

A second biochemical study is being done to examine the mechanism of action to nitrates and sulfates. The results of these studies should provide additional insight into comparative toxicity of these pollutants.

Studies are being conducted that employ interaction of pathogenic organisms and air pollutants to demonstrate increased susceptibility to infectious pneumonia. The model has been used effectively in environmental toxicological studies of ozone, NO_2, radiated automobile smog and exposure to some trace metals. The results have shown that the role of infectivity can be enhanced in certain species of animals studied.

The model has also been used to study mechanisms of action of pollutants. An important problem in NO_2 and O_3 toxicity involves relative toxicity of mode of dose-concentration or a function of time over given time periods. The results of these preliminary studies show greater mortality in experimental animals from pulmonary infection produced by the same concentration multiplied by time for different time periods (for example: 14 ppm x 0.5 hr. versus 1 ppm x 7 hr.). The study indicates that actual concentration has more influence than duration of exposure. An inverse relationship was found between survival and length of exposure at constant concentrations.

1.5.1.2 Carbon Monoxide--Both the present ambient air quality standard for carbon monoxide of 10 mg/m^3 (9 ppm) averaged over eight hours and of the 40 mg/m^3 (35 ppm) one-hour average coincide with carboxyhemoglobin levels of approximately 1.5%. Since the standard was established, new evidence has appeared supporting the current standard in three areas. These areas include:

(1) Effects on individuals with arteriosclerotic vascular disease (2.5-3.0% range during exercise); (2) effects on exercise capacity in

healthy individuals (diminished exercise performance at COHb levels of approximately 5-6%); and (3) additional evidence on alertness effects (impairments on vigilance tasks at COHb levels ranging from 3.0-6.5%).

1.5.1.3 Oxidants--The oxidant thresholds for cough and chest discomfort were found in one study to be 500-600 μg/m^3 as a maximum one-hour average. These levels are similar to those observed in studies of occupational exposure of men. These thresholds should be generally applicable to healthy adults and would probably represent an upper bound for persons with pre-existing cardiovascular disease or asthma.

The synergistic effect of ozone and sulfur dioxide on human pulmonary function has been reported in the past two years. There is also concern that interaction of these two pollutants on lung function is impaired in a non-linear fashion to any stimulus. The "extra" decrement attributed to the combination of SO_2 and ozone could be an additive effect in the non-linear part of lung-function curves.

Chromosome breaks in hamsters following ozone exposure have been observed. But this may only be a peripheral and not a stem cell effect. If so, it is not properly described as a mutagenic effect, but more data are needed to clarify this point.

There is much evidence that exposure to ozone at concentrations $\leq$1.0 ppm can produce physiological, biochemical and pathologic conditions in experimental animals. Pulmonary lesions have been frequently observed in experimental animals exposed to these levels. There is some evidence that the resultant damage is a function of time and dose of ozone expoure. Several studies have shown an effect on behavior patterns of experimental animals exposed to ozone concentrations below 1 ppm. A number of studies have shown that ozone exposure induces changes in pulmonary function.

Studies have consistently shown deleterious effects (decrease in pulmonary function, chest discomfort, cough and eye discomfort) in people exposed to less than 1 ppm (0.05 to 0.75 ppm). Healthy adult males exposed to 0.50 ppm of ozone for two hours during intermitten light exercise developed measurable physiological and biochemical changes.

1.5.1.4 Particulates--The theoretical definition of suspended fine particles as they relate to health are necessarily broad and somewhat arbitrary. Deposition of particles anywhere in the respiratory tract, from nose to alveoli, may be harmful to health. There appears, however, that non-viable particles deposited below the trachea may be more harmful than those deposited in the nasal cavity. Whether particles must reach the alveoli to exert harmful effects is a more controversial issue. It is likely that particles deposited in the bronchi or bronchioles are more important in producing bronchitis than those deposited in the alveoli. At present, there is little value in confining the category of suspended fine particles only to those particles that reach the alveoli.

The Task Group on Lung Dynamics has calculated that up to 10% of inhaled particles of diameter 2-5 μm are deposited in the alveolar compartment and up to 30% are deposited in the alveolar compartment. Most of the particles of diameter above 5 μm are deposited in the nasal cavity. So a size range of fine particulates, up to 2-5 μm diameter, measured aerodynamically, is of principal interest from a health standpoint.

The toxicological properties of inhaled particles are related to a complex of factors that include the specific physical-chemical properties of the particles themselves and host conditions that affect response to exposure to these particles. As for toxicity of certain specific particulates that may exist in the atmosphere, moderate amounts of information are known. But such information is not usually available in a form suitable for accurate assessment of minimum time-concentrates for exposure that will lead to adverse health effects.

Even less information is known about how physical environmental variables (weather conditions) may interact with suspended particulate matter and alter its chemical composition and affect its toxicity. Weather conditions per se may affect people in such a way as to alter their exposure to inhaled particulates. The information that is available, however, provides a basis for estimating the relative toxicity of certain substances and provide insight into problem areas where our information is inadequate.

The main way air particulates affect health is presumably through breathing and consequent effects on the respiratory system. This presumption is acceptable in determining short-term effects of irritant aerosols, but may be less tenable in considering long-term exposure effects where such responses are carcinogenesis, mutagenesis and subtle metabolic effects result from whole body burdens. In these cases, routes of entry besides breathing may be important in establishing dose-response relationships, However, inhaled particles may become non-respiratory toxicants where substances are translocated to the gastro-intestinal system by muco-ciliary transport and swallowing. There they may exert a primary toxic effect or be absorbed through the lung into the blood stream and translocated to other tissues, eliciting an adverse health effect.

Deposition rates and retention time of inhaled particles are separate phenomena with overlapping biologic effects. Particle retention time is dependent upon: (1) the site of initial deposition in the respiratory tract, and (2) the chemical composition and properties of the particles.

If particles are deposited in the ciliated epithelium of airways, particle clearance is reasonably rapid. Toxicity then depends on solubility of particles in mucus while in transit up the muco-ciliary escalator. If the particle is highly soluble, toxic inflammation in the airway epithelium may occur.

Particles deposited in the alveoli of the lung may only slowly clear from this location. The extent to which alveoli are cleared reflects their solubility and subsequent translocation via lymphatic drainage or macrophage phagocytosis and clearance via the muco-ciliary transport mechanisms.

In some cases, especially with fine suspended particle material, numbers of particles may be more relevant than particle mass. To relate the number of particles to the mass size distribution requires determination of frequency distribution. Particle number can be toxicologically important since the large surface area may promote gas-particle or volatile-substance particle interaction. Coupled with small size, these interactions may result in deeper penetration of gaseous or volatile substances in the respiratory tract and more rapid dissolution. Surface area is also important for highly insoluble particles that express their toxic potential only at the surface.

Another important factor in the regional deposition of inhaled particles is hygroscopicity. Particles, as usually measured externally, are not saturated with water. The growth of sodium chloride particles is a function of relative humidity, with particle size increasing when relative humidity exceeds 75%. The respiratory tract, with its saturated atmosphere, may considerably increase effective particle size over and above that measured in ambient air. However, hygroscopicity is of less significance with particles of high density.

1.5.1.5 Sulfur Oxides, Sulfuric Acid and Sulfate--One of the primary problems in determining health effects of SO_2 continues to be development of an understanding of the way this gas interacts with other substances in the atmosphere. Laboratory studies have demonstrated that, in an experimental situation, the levels of SO_2 found in ambient air are innocuous until combined with other substances.

Similar studies with animals demonstrated increased toxicities of sulfuric acid mists and various sulfate compounds that are products of atmospheric transformation of SO_2. The importance of high relative humidity (580%) to enhancement of the effect of sulfur dioxide and sodium chloride aerosol is demonstrated through sensitive respiratory physiologic responses. Observed initial associations of adverse health effects with ambient levels of suspended sulfates in epidemiologic studies tend to support these laboratory studies.

Studies of three New York neighborhoods showed that cold temperatures were directly related to increased symptom rates in people with combined heart and lung disease. Elevated suspended sulfates were the only pollutant consistently associated with symptom aggravation. Daily sulfur dioxide and total suspended particulate concentrations could not be associated with symptom aggravation in the "heart and lung" panel, the most sensitive to variations in daily pollutant concentrations.

Also, asthma attack rates were more consistently associated with daily suspended sulfate levels than with either sulfur dioxide or total suspended particulates.

Studies of daily asthma attack rates in the Salt Lake Basin showed that attacks were more consistently correlated with colder outdoor temperature than with any measured pollutant. So an analysis of asthma attack rates measured against daily pollutant concentrations was carried out within two ranges of minimum temperature, 30 to 50°F and greater than 50°F. Virtually no relationship between sulfur dioxide and attack rates appeared, but total suspended particulates and suspended sulfates were positively correlated with daily asthma attack rates. A higher frequency of asthma attacks was observed at the same daily total suspended particulate concentration when a high sulfate fraction was present in the atmosphere so that it appeared sulfate levels were a stronger determinant of asthma attack rates than total suspended particulates.

The breathing ability of elementary school children in New York City was affected in areas with high levels of SO_2. In Cincinnati, this same indicator was associated with sulfate exposure.

The pattern of chronic bronchitis rates is consistently higher among residents of more polluted communities.

1.5.1.6 Hydrocarbons--The National Ambient Air Quality Standard for hydrocarbons was established as a guide in regulating oxidant standards. The reference method measures gas-phase hydrocarbons corrected for methane. Particulate hydrocarbons, especially polynuclear hydrocarbons, were not considered in establishment of the standard. Current ambient air data are limited primarily to non-methane gaseous hydrocarbons and benzo-a-pyrene.

When the criteria document of hydrocarbons was published (March 1970), there was insufficient evidence to demonstrate any bad health effects from gaseous hydrocarbons at levels found in the ambient air. No new evidence to the contrary is available. However, little research has been done on the question.

Many gaseous hydrocarbons are directly involved in atmospheric formaldehyde, other aldehydes, ketones, peroxyacetyl nitrate (PAN) and other oxidants. Some of these products produce adverse health effects. A limited amount of study in cases of occupational exposure has been devoted to some of these compounds. In reported studies Hodgkin's disease has been associated with exposure to benzene at concentrations of 150 to 210 ppm in the work place. Toxic effects attributed to formaldehyde concentrations of 2 to 10 ppm have been reported. A study of the incidence of leukemia involving petroleum and chemical products in the work population produced no conclusive increased risks. The limitations inherent in each of these studies are such that results should be viewed with caution--particularly for quantitative results.

Occupational evidence and laboratory experiments for other classes of hydrocarbons such as PVC/VC, PCB's and polynuclear hydrocarbons show that some of these compounds are carcinogenic. The dose response data, however, are incomplete.

1.5.1.7 Mercury--Several recent animal exposure studies using methyl mercury given in repeated oral doses over relatively long time-periods show that a "no-effect" level for neurological sign development and/or histopathological evidence of mercury poisoning is from 0.03 mg/kg body weight (monkeys, cats) to 0.1 mg/kg body weight (calves).

Daily oral doses of alkyl-mercury compounds as small as 0.4 mg/kg body weight produce neurological disorders in rabbits, cats and dogs. Daily oral doses of 0.25 mg/kg body weight of methyl mercuric chloride given throughout most of the gestational period have caused increased abortions and fetal abnormalities in cats. Levels above 0.3 mg/kg given during gestation also increased fetal abnormalities in rat fetuses.

Most animal experiments were carried out with daily dose levels much higher than the foregoing experiments. The most chronic exposure found was that of monkeys exposed for two years. Low level, long-term exposures were notably absent.

Behavioral changes have been produced in rodents where no histological lesions were found from single oral doses of methylmercuric chloride. A relatively high 25 mg/kg dose level was required since doses at 20 mg/kg level did not produce significant changes.

1.5.1.8 Beryllium--A long latent period of 15 or more years has been observed between the onset of disease and the last exposure to beryllium, with evidence indicating that beryllium may accumulate in a latent form in lyosome. A latent period could persist for years until declining adrenal stress, reserve and output with age caused lyosomal instability and the onset of beryllium disease. Under these conditions, especially if the adrenal reserve was also low, the adrenal output may not be adequate to meet the needs.

In recent experiments, the biological half-life of ^{7}Be in mice was found to be about twice the value cited by the ICRP (540 days). There is now some evidence of auto-immune response subsequent to beryllium exposure.

1.5.1.9 Asbestos--The association of impaired health with industrial exposure to asbestos, principally asbestosis and pulmonary cancer is well known. There is little evidence that exposures to low levels of asbestos and asbestos-like fibers that may be present in ambient air have resulted in either asbestosis or pulmonary cancer in people. However, the discovery of mesiothelioma of the pleura associated with low exposure or casual contact with chrysotile asbestos has raised suspicion about possible health hazards of air pollution.

Evidence indicates that all major types of asbestos may cause lung cancer. There are clear differences in risk with type of filter and the nature of exposure, however. All commercial types of asbestos, except anthophylite, may cause induction of mesathelioma. However, the risk is greatest with crocidalite, less with amosite and apparently less with chrysotile.

Some cases of mesothelioma have no known association with exposure to asbestos. There is some evidence of association of mesothelioma development with air pollution near croidalite mines and factories working with mixed fibers. There appears to be no extra risk from air pollution near chrysotile and amosite mines.

At present, there is no evidence of extra cancer risk to the general public from asbestos in air, water or food. Cigarette smoking enhances the risk of developing bronchogenic cancer in workers exposed to asbestos. There is evidence that health effects associated with exposure to asbestos may not be unique to commercial forms, but may also be associ- with asbestos-like fibers found in other rocks and possibly man-made fibers.

1.5.2 Materials

The soiling effects of particulate matter and most cause-effect relationships for common gaseous pollutants have long been known. What has been lacking is information on dose-response relationships to use in cost-benefit studies, support for primary air quality standards and setting of secondary standards.

In past years, EPA scientists have conducted both laboratory and field studies to better define cause-and-effect. Recently they used specially-designed controlled environment chambers to generate needed dose-response data for economically vulnerable materials. Although some preliminary information was produced, all (materials) research for FY-75 and after, including dose-response studies, was terminated because of budget limitations.

1.5.2.1 Nitrogen Oxides--The damaging effects of atmospheric nitrogen oxides mainly concern the textile industry. Nitrogen dioxide (NO_2) is the troublesome pollutant; nitric oxide (NO) appears harmless. Atmospheric NO_2 can react with a number of textile dyes and produce noticeable color change or fading, causing a problem to the textile industry for decades. Concerning the yellow discoloration of undyedwhite and pastel-colored fabrics, chemists have traced this problem to the action of NO_2 on additives used to enhance fabric marketing properties. In the United States, annual gross damage to materials by NO_2 is estimated at three-quarters of a billion dollars.

1.5.2.2 Sulfur Oxide--The fact that SO_2 speeds deterioration of many materials has long been recognized. Both field and laboratory studies have shown that SO_2-polluted environments (1) increase the corrosion rates of most metals, especially iron, steel and zinc; (2) damage building materials such as limestone, marble, roofing slate and mortar; (3) discolor and cause deterioration of statuary and other works of art; (4) increase erosion rates of oil base paints; (5) degrade textile fibers, especially cotton and nylon and fade-dyed fabrics; (6) embrittle and discolor paper and (7) weaken leather.

1.5.2.3 Ozone--Damage by atmospheric ozone occurs mainly to elastomers and textile dyes. Not all elastomers, however, are subject to ozone damage; synthetic elastomers with saturated chemical structures have inherent resistance, although they are relatively expensive and account for only a fraction of the market. The great bulk of elastomers, including natural rubber and synthetic polymers of styrerebutadiene, polybutadiene and polyisoprene, contain double bonds prone to oxidation and thus sensitive to ozone. Researchers have developed antiozone additives capable of protecting elastomers, but such protection is not permanent. For certain items, such as tires, it usually lasts for the life of the item.

Some important textile dyes are susceptible to fading from ozone exposure. Blue dyes used on acetate and polyester/cotton fabrics and nylon carpets have been particularly troublesome. To prevent or mitigate ozone fading, the textile industry must use more resistant dyes and/or inhibitors, increasing the cost of finished goods.

1.5.3 Ecology

1.5.3.1 Nitrogen Compounds--The effect of nitrogen oxides on vegetation has been noticed only near industrial sources, as in the effect of nitric acid on plants where ambient levels of nitrogen dioxide have been high. Effects have been identified chiefly through laboratory experiments. Indirect damage to vegetation has occurred from formation of acid rain and photochemical reactions.

Photochemical reactions result in the formation of peroxyacyl nitrate, the most abundant of the compounds formed, and responsible for serious plant damage.

1.6 CONTROL TECHNOLOGY

1.6.1 Stationary Sources

Stationary combustion sources contribute more to the ambient atmospheric loading of SO_x, NO_x and total suspended particulates (TSP) than any other anthropogenic category, causing approximately 80% of SO_x emissions, 50% of NO_x emissions, and 50% of ambient fine particulates.

Advances in the development of technology to control SO_x, NO_x and primary particulates have been achieved, and additional improvements are expected in coming years.

Industrial processes and open sources (e.g., open burning, mining, incineration, fugitive emissions) account for approximately 16% of SO_x emissions, 44% of hydrocarbon emissions, 22% of CO emissions and 25% of ambient fine particulates. They are also responsible for most hazardous air pollutant emissions (i.e., asbestos, beryllium and mercury) as well as vinyl chloride and other potentially hazardous carcinogenic pollutants.

1.6.1.1 Particulate Control--Most pressing is the development of commercially available and widely applicable fine particle (less than 3 microns) control technology. It is currently in very early development under EPA sponsorship. This technology is also needed to control detrimental trace metals.

Scrubbers, electrostatic precipitators and fabric filter collectors are the principal particulate collection devices. They are being improved by attention to lowering costs, increasing their applicability and extending the range of collection to smaller particle sizes. In addition, entirely new concepts of particle collection are being investigated.

System studies have been completed for each conventional device to define areas for improvement and show new applications. Long-range projects include: development of models for existing collectors; identification and laboratory testing of new concepts in particle technology and new work in small particle detection and generation equipment.

1.6.1.2 Sulfur Oxides Control--In the area of sulfur oxides control, achievement of Ambient Air Quality Standards demands control of industrial combustion, industrial processes and area sources as well as utility combustion. Natural low-sulfur fuels are only sufficient for about 40% of the demand of State Implementation Plans. The remainder must be supplied by technology in the form of effluent desulfurization, fuel cleaning or process modification. Although the currently defined sulfur oxides control technology program contains projects diverse enough to ensure achievement of Ambient Air Quality Standards, substantial EPA research and development investment will be required to bring this technology to commercial fruition. Only effluent desulfurization technology for electric utilitlies should achieve widespread commercialization within the next few years.

Although the program has emphasized stack gas cleaning systems, with five or six such processes to be demonstrated before 1976, it has also included work in areas of fuel modification and desulfurization, industrial process modification and advanced combustion processes.

Most of EPA's early coal desulfurization work was to evaluate and improve physical cleaning methods for coal. These methods should now have moderate applicability in reducing sulfur by 30 to 70% in certain coals. Ongoing work here includes washability testing, coal desulfurization and cleaning and pollutant control evaluation and optimization. Most recent work is aimed at chemical desulfurization and the problems of pollutants in fossil fuel.

Laboratory-scale work is under way on processes to remove sulfur totally from coal. The two processes under development are unique since one is completely selective to inorganic sulfur in coal and the other is preferential organic sulfur removal, but both produce a solid fuel retaining the basic physical characteristics of coal. The technical feasibility of the inorganic sulfur removal system has been proven on the laboratory and bench scale and is undergoing design to a pilot-plant-size operation, with construction of this plant planned for early 1974. The degree of sulfur removal from the organic process is currently being studied in a laboratory apparatus and should be adequately developed by mid-1974 to start scale-up design to continuous pilot operation by September 1974. The two systems will be examined in detail as to possible integration into one scheme for complete removal of sulfur from coal. After successful pilot plant operation, plans call for scale-up to a demonstration-size plant.

Two factors--the major contribution of small coal-and-oil-burning sources (area sources) to the pollution of ambient air and severely limited supplies of low-sulfur fuels--indicate a need for clean fuel or coal conversion processes. EPA has provided funds to both the bureau of Mines and the Office of Coal Research to help develop conversion and gasification processes for providing clean fuels and help determine the environmental controls these techniques will require.

Work on advanced processes involves primarily the development of fluidized-bed combustion. Fluidized-bed combustion options include: pressurized coal combustion, coal gasification for the production of low-sulfur, low-Btu gas and oil gasification. EPA also has conducted systems studies for the development of advanced power cycles.

Work is also under way to control emissions from smelters, iron and steel operations, Kraft wood pulping, iron foundries, secondary aluminum furnaces and other industrial sources.

1.6.1.3 Nitrogen Oxides Control--On a national basis, 98% of the nitrogen oxides (NO_x) from stationary sources are from combustion processes. Combustion control technologies under EPA investigation include: combustion modifications such as flue gas recirculation, off-stoichiometric combustion and low excess air operation; identification of alternate or novel combustion systems with inherently low NO_x emission levels; changes in burner design and use of alternate fuels. Although flue gas cleaning processes and advanced power cycles are also being investigated, they may offer only longer-term solutions to the problem. Major emphasis has been on coal combustion in utility and industrial boilers, since this poses the most difficult problem.

The main approach has been modification of the combustion process to reduce NO_x formation, with bench-scale and field work indicating that control for the immediate future can be achieved. In addition, promising stack gas cleaning processes are being investigated on a small scale. Results in this area are not too encouraging to date, however.

A complicating factor is that NO_x are formed during combustion through two separate mechanisms--the fixation of nitrogen in combustion air, and the conversion of fuel-bound nitrogren contained in the fuels. Although some control of both mechanisms has been achieved by combustion modifications, it remains to be determined whether or not combustion modification alone will adequately control the NO_x from fuel nitrogen.

1.6.1.4 Hazardous and Other Control--The number of pollutants requiring control has expanded to include more than 30 potentially harmful and annoying air pollutants. Since most of them are likely to be emitted as particulate matter, there is strong interaction between these two programs. Hazardous and other pollutants under consideration include: asbestos, beryllium, cadmium, carbon monoxide, fluorides, hydrocarbons, lead, mercury, and odorous materials from rendering plants, pulp mills, sewage treatment plants and chemical process industries. Because of the paucity of data now available, many problem definition and source characterization studies are required.

2. INTRODUCTION

National Ambient Air Quality Standards established under the provisions of the Clean Air Act amendments of 1970 were designed on the basis of the best available information. Since this information was incomplete, the Environmental Protection Agency began a continuing research program to improve the data base and assess its adequacy. This document is the first in a series of annual reviews by the Environmental Research Center/RTP, as to results of its research efforts. It is not intended to be a update of the criteria documents, which will be accomplished under the Pollutant Characterization Program.

Since this is the first of a series of reviews, it must cover new information attained by ERC/RTP since promulgation of the Standards. A review of the basis for the National Ambient Air Quality Standards and automobile emission controls has recently been completed by the National Academy of Sciences (NAS). For convenience, some material presented here duplicates that presented by NAS.

Maintaining air quality and the consequences for human health and welfare involves understanding many scientific, economic and social variables. Since our present understanding is extremely limited, standard-setting and environmental control must be based in large measure on judgment. Man-made environmental pollution is a consequence of our unwillingness or inability to control human population and the products of our natural resources, so that decisions on control are compromises with impact on all of society's values. There is an important element of risk resulting from incomplete information and understanding.

Material presented here represents only a small part of the problem. It is limited by our ability to: (1) measure gaseous and aerosol compounds which have been classified as deleterious or hazardous; (2) quantify and characterize emissions of pollutants from stationary and mobile sources; (3) monitor and characterize atmospheric loading; (4) determine the effects of a polluted atmosphere on human health and welfare and (5) control man-made emissions necessary to maintain a given air quality.

3. MEASUREMENT

3.1 INTRODUCTION

Measurement of an air pollutant begins with isolation and identification. This is the qualitative step. Technique is developed to generate the known substance in a controlled atmosphere free of unknown substances. The quality of a sensor is then judged based on freedom from response to other substances, sensitivity to the substance to be measured and other characteristics.

Equally important is how well the measuring method reflects concentrations of the substance sensed. This is the quantitative step. Before assessing the quantitative capability of a method, it is essential to generate a substance in known concentrations. Determining the response of a sensor to a series of known concentrations constitutes the calibration of the sensor. The degree to which the sensor reproduces the calibration reflects the stability of the methods.

The scope of the measurement problem is shown in discussion following.

The composition of unpolluted air is not known precisely, but Table 3.1 represents an approximation.

Table 3.1. APPROXIMATION OF THE GASEOUS COMPOSITION OF DRY UNPOLLUTED AIR

Constituent	Molecular Formula	Volume Fraction
Nitrogen	N_2	78.09%
Oxygen	O_2	20.94%
Water	H_2O	--
Argon	Ar	0.93%
Carbon Dioxide	CO_2	0.0318%
Neon	Ne	18 ppm
Helim	He	5.2 ppm
Methane	CH_4	1.0-1.2 ppm
Krypton	Kr	1.1 ppm
Nitrous Oxide	N_2O	0.5 ppm
Hydrogen	H_2	0.5 ppm
Carbon Monoxide	CO	0.1 ppm
Xenon	Xe	0.09 ppm
Ozone	O_3	0.02 ppm
Organic Vapors	--	~0.02 ppm
Sulfur Dioxide	SO_2	~0.001 ppm
Nitrogen Dioxide	NO_2	~0.001 ppm
Ammonia	NH_3	~0.001 ppm

Major gases and vapors produced by man are shown in Table 3.2.

Table 3.2. PRIMARY GASES AND VAPORS PRODUCED BY HUMAN ACTIVITIES

Compound	Formula
Carbon dioxide	CO_2
Carbon monoxide	CO
Sulfur dioxide	SO_2
Nitric oxide	NO
Hydrogen sulfide	H_2S
Ammonia	NH_3
Hydrogen chloride	HCl
Hydrogen fluoride	HF
Paraffins	--
Olefins	--
Aromatics	--

Principal secondary pollutants produced in the atmosphere are shown in Table 3.3.

Table 3.3. SECONDARY ATMOSPHERIC POLLUTANTS

Compound	Formula
Nitrogen dioxide	NO_2
Ozone	O_3
Peroxyacetyl nitrate	$H_3C\text{-}C\text{-}\ddot{O}\text{-}O\text{-}NO_2$
Aldehydes	$RCHO$
Sulfuric acid	H_2SO_4

Organic or inorganic particles found in the atmosphere frequently are participants in the formation of gaseous or particulate secondary pollutants shown in Table 3.4.

Table 3.4. ATMOSPHERIC PARTICULATES AND MAJOR PRIMARY AND SECONDARY AIR POLLUTANTS FORMED BY PARTICLE PARTICIPATION

- Suspended Particulate Matter
  - Inorganics
    - Metals, (Pb, Cd, Be, Hg, etc)
    - Fluorides
    - Nitrates, Sulfates, Phosphates
    - Asbestos
    - Mineral Dusts (Silicates, Silica, etc)
  - Organics
    - Polycyclic Organics (Benzo [a] pyrene, etc)
    - Oxygenated Compounds
    - Pesticides
    - Aeroallergens
  - Gases
    - Inorganics
      - Sulfur Oxides (SO_2, SO_3)
      - Nitrogen Oxides (NO, NO_2)
      - O_3
      - CO
      - H_2S
      - HCl, Cl_2, Fluorides, etc

Table 3.4 (continued)

- Ammonium Compounds (NH_3, etc)
- CO_2

Organics

- Hydrocarbons (Paraffins, Olefins, Aromatics)
- Oxygenated Compounds (Aldehydes, Ketones)
- Sulfur Containing Compounds (Mercaptans, etc)
- Nitrogen Containing Compounds (Peroxyacetyl Nitrate (PAN), etc)
- Halogenated Compounds

Table 3.5 shows pollutants for which the federal government has established National Ambient Air Quality Standards

Table 3.5. NATIONAL AIR QUALITY STANDARDS[a]

Pollutant	Averaging Time	Primary[b] Standards	Secondary[c] Standards	Reference[d] Method
Sulfur Dioxide	Annual Arithmetic Mean	80 $\mu g/m^3$ (0.03 ppm)	--	Pararosaniline Method
	24 hours	365 $\mu g/m^3$ (0.14 ppm)	--	
	3 hours	--	1300 $\mu g/m^3$ (0.5 ppm)	
Particulate Matter	Annual Geometric Mean	75 $\mu g/m^3$	60 $\mu g/m$	High Volume Sampling Method
	24 hours	260 $\mu g/m^3$	150 $\mu g/m^3$	
Carbon Monoxide	8 hours	10 mg/m^3 (9 ppm)	Same as Primary Standards	Non-Dispersive Infrared Spectroscopy
	1 hour	40 mg/m^3 (35 ppm)		
Photochemical Oxidants (corrected for NO_2 and SO_2)	1 hour	160 $\mu g/m$ (0.08 ppm)	Same as Primary Standard	Gas Phase Chemiluminescent Method
Hydrocarbons (corrected for methane)	3 hours	160 $\mu g/m$ (0.24 ppm)	Same as Primary Standard	Flame Ionization Detection Using Gas Chromatography
Nitrogen Dioxide	Annual Arithmetic Mean	100 $\mu g/m^3$ (0.05 ppm)	Same as Primary Standard	New Reference Method Under Study

Table 3.5 (continued)

a. National standards other than those based on annual arithmetic means or annual geometric means are not to be exceeded more than once per year.

b. National Primary Standards: The levels of air quality necessary, with an adequate margin of safety, to protect the public health.

c. National Secondary Standards: The levels of air quality necessary to protect the public welfare from any known or anticipated adverse effects of a pollutant.

d. Reference method as described by the EPA. An "equivalent method" means any method of sampling and analysis which can be demonstrated to the EPA to have a "consistent relationship to the reference method."

e. For use as a guideline in assessing implementation plans.

EPA plans to examine emissions from industrial categories that may lead to additional standards. Stationary sources under consideration are:

*Aluminum Reduction Plants
Animal Feed Defluorination Plants
Automobile Assembly Plants
Chlorine and Caustic Plants
*Coal Cleaning Plants
Coke Plants
*Copper Smelters
Cotton Gins
*Ferro-Alloy Plants
Gas Turbines
Grain Millins and Handling
Graphic Arts Plants
Grey Iron Foundries
Hydrochloric Acid Plants
Lime Plants
Paint and Varnish Plants
Petrochemical Plants
*Phosphate Fertilizer Plants
*Phosphoric Acid Plants
*Phosphorous Reduction Plants
Pulp and Paper Mills
Rendering Plants
*Sewage Sludge Incinerators
Soap and Detergent Manufacturing Facilities
Sulfur Recovery Units
Vinyl Chloride Plants
*Zinc Smelters

*Promulgated or proposed.

Emission standards for asbestos, beryllium and mercury are contained in Federal Register 38 (6) 8820, April 6, 1973. These substances have been identified as hazardous air pollutants under the Clean Air Act as amended.

In 1970 Congress passed legislation requiring 1975 automobiles to show a 90% reduction in hydrocarbon and carbon monoxide emissions over 1970 models and a reduction in nitrogen oxide emissions by 1976 of 90% from that in 1971 models. Regulations covering 1972-1975 light duty vehicles and heavy duty engines were published in Federal Register 37 (22) 24250, November 15, 1972, and amended in Federal Register 38 (124), June 28, 1973. The Administrator granted a one-year extension for the 1975 standard in Federal Register 38 (126) 17441, July 2, 1973, and a one-year extension for the 1976 NO_x standard in Federal Register 38 (161) 22474, August 21, 1973.

Additional regulations for special engine types beginning with 1973 model year are contained in Federal Register 37 (221) 24250, November 15, 1972, and interim standards for specific truck types in Federal Register 38 (151) 21398, August 7, 1973.

Standards for control of air pollution from aircraft and aircraft engines were promulgated by EPA in Federal Register 38 (136) 19088, July 17, 1973.

Thus far EPA has promulgated methods for measuring six ambient air pollutants, one of which (NO) has been rescinded for further study; five pollutants for five sources under standards for new stationary sources, two hazardous pollutants and four pollutants from mobile sources.

The objective of the Clean Air Act is ensuring air quality. Since knowledge of atmospheric loading is important to air quality, it is to this subject that the rest of this section will be largely devoted. Generation of a controlled atmosphere for purposes of studying performance characteristics and establishing calibration of a manual or instrumental method will be covered. Measurement methods in common use as well as those having promise will be discussed as well as EPA efforts to upgrade measurement methods by promulgating performance criteria for reference and equivalent methods. Validation techniques, auditing and interlaboratory and intralaboratory evaluation methods will be discussed.

3.2 PRODUCTION OF TEST ATMOSPHERES

The adequacy of a manual or instrumental method designed to measure a gaseous pollutant is proven by the manner in which it respons to a test atmosphere artifically produced by introducing into clean air a known amount of the pollutant. Knowing the volume of clean air (diluent gas) and the volume of the pollutant, the volume-to-volume relationship can be calculated. In ambient air measurements this is commonly referred to in terms of parts per million (ppm), parts per hundred million (pphm) or parts per billion (ppb) by volume. Air pollution technologists assume the "by volume."

The reading obtained as a result of the signal (the pollutant) is then a measure of the sensitivity of the method.

The same procedure is used for generating a test atmosphere that contains an interferent separately or in addition to the pollutant to be measured.

There is no technique for providing an optimal test atmosphere for all measurement methods used in ambient monitoring.

The permeation technique as originally reported described how a condensible gas (in its liquid state) would be sealed in a section of inert plastic tubing. Following an initiation period of a few hours to several weeks, permeation of the substance through the tubing proceeds at a constant rate until the enclosed gas is nearly exhausted. The rate of permeation is calculated by gravimetric determinations of weight loss in a unit of time. Using apparatus to control the temperature of the permeation tube and regulate the flow of the diluent gas stream over the tube, a wide range of known concentrations are obtainable from parts per billion to parts per million with achievable accuracies of within plus or minus 2%. The concept has been extended to include the controlled dispensing of non-liquifiable gases, and some instrument suppliers are including permeation dispensing devices as a self-contained calibration source or an optional ancillary module.

There are installations where gas mixtures pressurized in metal cylinders have advantages. Methane in air is an example of convenience dictating the use of a certified concentration of the gas for calibration of hydrocarbon analyzers. While not long ago the reliability of such specialized gas mixtures left much to be desired, recently specialty gases from industrial suppliers have improved greatly. Nonetheless EPA plans a quality control program for these mixtures.

The National Bureau of Standards (NBS) is more and more supplying standard gases for use in air pollution laboratories. Currently it supplies nitric oxide, carbon monoxide and methane in nitrogen at one or more concentrations. These concentrations are considerably higher than those found in the average atmosphere. The use of nitrogen rather than air as the diluent gas renders the mixture unusable for certain applications. NBS is cooperating with EPA in exploring the feasibility of supplying a greater variety of gases and concentrations and the use of air as a diluent.

Very promising is the use of aluminum cylinders for pressurized gases. Preliminary evidence indicates that changes to a contained gas due to wall effects occur at a much slower rate (if at all) in aluminum rather than steel cylinders. It has been established that aluminum cylinders are superior for storage of ultrapure air, a supply of which becomes increasingly important as measurement technology progresses. Having a pollutant-free gas for use as a diluent to provide step concentrations of a pollutant is useful in producing a calibration curve characterizing the response of any manual or automated method.

3.3 OXIDES OF NITROGEN MEASUREMENTS

3.3.1 Ambient Air

This section discusses the measurement of nitric oxide (NO), nitrogen dioxide (NO_2) and total oxides of nitrogen (NO_x). Most man-made nitrogen oxides are in the form of NO. In the atmosphere, NO reacts to form the more irritating and toxic NO_2. Other oxides of nitrogen, nitrogen pentoxide (N_2O_5), nitrogen tetroxide (N_2O_3) and nitrogen trioxide (N_2O_3) are present in the atmosphere in extremely low concentrations if at all. Their involvement in photochemical reaction is possible. Laughing gas, nitrous oxide (N_2O), if present in the atmosphere, is harmless. NO and NO_2, referred together as NO_x, are the compounds of primary interest.

3.3.1.1 Calibration--Permeation tubes are the preferred source for calibration of NO_2 analyzers. NO is supplied in nitrogen, typically at concentrations of 50 or 100 ppm, in pressurized cylinders. The concentration in the cylinders remains stable for months.

The calibration accuracy of NO_x analyzers is dependent upon a true zero. Residual NO and NO_2 are removed by converting the NO to NO_2 using ozone to oxidize the NO and then removing the NO_2 by an NO_2 absorbent like activated charcoal.

3.3.1.2 Manual Measurement--Manual NO_2 analytical techniques usually are performed in a laboratory remote from the sampling site; hence the requirement for a method to efficiently collect and retain the NO_2 samples. The sampling time is generally 24 hours. Variables are sampling rates, duration of sampling period, collection efficiency and analytical method. Absorption in liquids is the most common method of sampling.

3.3.1.2.1 Jacobs Hochheiser Method--This method, contained in Federal Register 36 (84) 8186, April 30, 1971, is a procedure where an ambient sample containing NO_2 is drawn through an aqueous sodium hydroxide solution producing a nitrite ion from NO_2. The resulting alkaline solution is treated in the laboratory to produce a color proportional to the NO_2 sampled so that optical absorbance is linearly proportional to the concentration of the colored species and is measured spectrophotometrically.

This method, declared the reference method for measurement of NO_2, was used in the National Air Sampling Network (NASN). However, in 1972, EPA studies of the procedure showed nonlinearity of collection efficiency varying from approximately 15 to 70%, depending on the concentration of NO_2 sampled. It was also found that NO in the presence of NO_2 caused a positive interference in the measurement.

EPA published the following remarks on June 8, 1973:

> ".....EPA's analysis indicates that the reference method is deficient in two respects. First, the method overestimates nitrogen dioxide concentrations at low levels and underestimates them at high levels because the collection efficiency of the abosrbing reagent is dependent upon nitrogen dioxide concentration being measured. Second, the method is subject to positive interference by nitric oxide. Since the variable collection efficiency problem cannot be resolved, this method can no longer serve as the reference method."

3.3.1.2.2 Saltzman Method--One of the most widely used chemical methods for determining NO_2 in ambient air is also known as the Greiss-Saltzman method. This colorimetric method is based on the reaction of NO_2 with sulfanilic acid to form a diazonium salt which couples with N-(1-naphthyl)-ethylene-diamine dihydrochloride to give a red dye. The color is measured spectrophotometrically at 550 nm and the value obtained is proportional to the NO_2 concentration.

This method is sensitive from 0.005 ppm to about 5 ppm when sampling is conducted with bubblers. Sampling time is usually 10 to 30 minutes.

The Intersociety Committee (ISC) has adopted the Saltzman method as the tentative manual method of analysis for NO_2. The American Society for Testing and Materials (ASTM) has also selected the Saltzman method as the standard method of test for nitrogen dioxide content of the atmosphere.

Ordinarily interferences are not a problem. A tenfold ratio of SO_2 to NO_2 produces no effect. A 30-fold ratio bleaches the color to a slight extent. Interferences from other oxides of nitrogen and ozone at typical ambient levels are negligible. Peroxyacetylnitrate (PAN) can give a response of up to 35% of an equivalent molar concentration of NO_2, but in ordinary ambient air, PAN concentrations are too low to cause any significant error.

The Saltzman method for NO_2 measurement cannot be used successfully when the delay between sample collection and color measurement is more than four to six hours or when sampling periods of longer than one hour are required because of color fading.

3.3.1.2.3 Tentative Method for the Determination of Nitrogen--Dioxide TGS ANSA--This method has its basis in the Levaggi (TEA) Method. It is currently one of several prime candidates for a reference method.

NO_2 is drawn through a solution of triethanolamine, o-methoxyphenol and sodium metabisulfite. The nitrite ion produced during sampling is determined colorimetrically by reacting the exposed absorbing reagent with sulfanilomide and 8-anilino-1-naphthralenesulfonic acid. The method is applicable to collections of 24-hour samples in the field followed by analysis within three weeks in the laboratory. The range of analysis is about 0.01 to 2 ppm. Beer's law is obeyed throughout this range. The method has a predictable collection efficiency of between 92-94% from 20-740 $\mu g/m^3$ NO_2 and virtually no interference from NO, SO_2, O_3 and CO_2.

3.3.1.2.4 Tentative method for the determination of nitrogen dioxide in the atmosphere (Sodium arsenite procedure)--This method has its basis in the Christie (arsenite) Method. It is also under investigation and is a prime candidate for the reference method.

NO_2 is drawn through a solution of sodium hydoxide sodium arsenite to form a stable solution of sodium nitrite. The nitrite ion produced during sampling is reacted with phosphoric acid, sulfanilamide and

N-1-(naphthyl) ethylenediamine dihydrochloride to form an azo dye. The method is applicable to collection of 24-hour samples in the field followed by analysis in the laboratory within six weeks. The range of analysis is about 0.015 to 1.0 ppm. Beer's law is obeyed through this range.

3.3.1.3 Automated Analyses--Commercially available instruments for the automatic analysis of NO_x are based on perhaps a dozen principles. Some of these are colorimetric, amperometric, ion-selective electrode, electrochemical, chemiluminescence and a variety of spectrometric techniques. The cost range is from about $1,000 to more than $10,000, with a size range from a portable 7 kilogram module to a room-sized, stationary 450 kilogram system. Skill required to operate an analyzer varies greatly. Selected analyzers suitable for ambient air field monitoring applications are discussed here. Complex techniques limited to the laboratory or special field applications are not included even though they may have superior performance characteristics. Also, certain promising field techniques such as second derivative spectrometers are excluded here owing to insufficient performance information, too rigorous operational requirements or too few instruments sold.

Analyzers representing breakthroughs in the art of measurement are coming to the forefront but have not been proven.

3.3.1.3.1 Colorimetric analyzers--Colorimetric analyzers usually represent automating of a manual technique. As with manual methods, such analyzers measure the optical absorbance of a solution following reaction with NO_2 in an air sample. The absorbance is linearly proportional to concentration of the colored species.

This type of anlayzer has been in use for nearly 20 years; improvement lately has been in the area of modifications to reagents, improved electronics, updated optics and so on.

Ten or more manufacturers are selling these analyzers, and an automated colorimetric method is under consideration for a reference method. Currently colorimetric analyzers are the most prevalent instrument for measuring NO_2, NO and NO_x although the chemiluminescent method is rapidly growing in usage. Advantages of colorimetric analyzers are simplicity, high sensitivity, and with effect controls, specificity. Problems include reagents leaking at fittings, temperature and pH sensitivity, long response time, reagent purity and interferents in the sampled air.

Analyzers almost exclusively use a modified Saltzman absorbing reagent.

Colorimetric NO_x anlayzers are designed to operate in one of three modes: series, parallel and simultaneous.

3.3.1.3.1.1 Series mode--The air sample is drawn through the reagent wherein NO_2 reacts to form the azo-dye which is measured and recorded as NO_2. The sample stream still containing NO passes through an oxidizer (e.g., acid permanganate bubbler) becoming NO_2 and is then measured. If the analyzer is properly calibrated, an accurate reading of NO_2 and NO is recorded. Summing the two readings provides the NO_x value.

3.3.1.3.1.2 Parallel mode--The air sample is drawn into the analyzer where it is split. One flow is passed through the reagent where the NO_2 reacts to form the azo-dye which is measured and recorded. The other stream is drawn through an oxidizer where the NO is converted to NO_2. The NO_2 present in the sample stream plus the NO (now NO_2) reacts to form the azo-dye which is measured and recorded. This reading is the NO_x value (NO_2 + NO). By subtracting the NO_2 reading the NO value is obtained. Again, the best results are obtained by a dynamically calibrated analyzer.

3.3.1.3.1.3 Simultaneous mode--The air stream is split into two portions as it is drawn through the anlyzer. One stream is scrubbed of its NO_2 content by drawing it through a filter containing triethanlomine (TEA) impregnated on firebrick for the removal of NO_2 which reacts with the azo-dye which is measured for the NO reading. The other stream is drawn through the reagent where the NO_2 reacts and the azo-dye developed is measured and recorded as NO_2. Combining the two readings gives the NO_x value.

Each of three modes has certain advantages and disadvantages. Generally an instrument using one of the modes, properly attended, maintained and most important, carefully calibrated, will provide creditable data. Electronic modules can be added to the systems for a variety of signal presentation such as direct digital readings of NO, NO_2 and NO_x.

3.3.1.3.2 Chemiluminescent analyzers--EPA has under consideration the chemiluminescent method as a reference method for NO_2. Approximately seven years ago, EPA inaugurated in-house and contract investigations into measuring oxides of nitrogen by application of chemiluminescent technology. Light energy--with or without flames--of specific wavelengths can be generated by bringing into a chamber a given substance that burns or reacts with another substance to emit light energy detected by a photomultiplier tube. Application of the principle of measurement for oxides of nitrogent has passed through several stages.

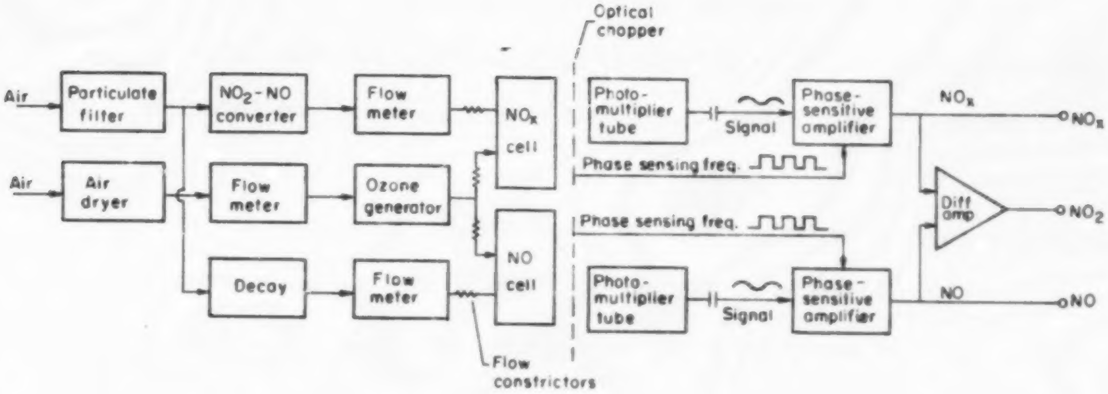
Today about ten manufacturers are selling oxides of nitrogen analyzers using the chemiluminescent principle. They operate over a wide range of ambient temperature and humidity with minimal effect on accuracy.

The oxides of nitrogen analyzer is designed to measure NO, NO_2 and NO_x in a continuously exchanged ambient air sample. The system reacts quickly to quantitative changes in NO, NO_2 and NO_x content of the sample, while providing a highly stabilized measurement capability for extended periods without repeated adjustments. An output signal proportional to the measurement is produced for recording.

The oxides of nitrogen analyzer uses the principle of photometric detection of chemiluminescence resulting from the flameless gas phase reaction of NO with ozone (O_3). Since this reaction only occurs between NO and O_3, the amount of NO_2 is shown by the difference between NO_x and NO, accomplished by dividing the input sample into two flow streams. One stream goes directly into the reaction chamber and results in a measurement of NO. The other stream, defined as NO_x, goes through a catalytic converter changing NO_2 to NO but having no effect on incoming NO, and then into the reaction chamber for measurement. The amount of NO_2 is determined by subtracting the NO from the NO_x measurement. The analyzer provides automatic cycling through the NO and NO_x measurements with the output difference (NO_2) up-dated after each cycle. The normal cycle time is one or two minutes.

Analyzers generally have several ranges. In most cases a range is 0-0.5 ppm full scale with a minimum detectable sensitivity of 5 ppb. Zero and span drift usually do not exceed one percent in 24 hours. Nominal weight of the instrument is 25 kg.

The variation produced by one manufacturer is shown in Figure 3.1. This analyzer measures NO and NO_x simultaneously by using two cells, negating the necessity for cycling between measurements. The manufacturer claims improved stability with use of the optical chopper for automated drift compensation and an improved NO_2 to NO converter. The EPA St. Louis Regional Air Pollution Study (RAPS) has 25 such analyzers in the Regional Air Monitoring Stations (RAMS). As of November 1974 they are undergoing the Systems Acceptance Test (SAT).



Optical chopper
Air
Particulate filter
NO2-NO converter
Flow meter
NOx cell
Photo-multiplier tube
Signal
Phase-sensitive amplifier
NOx
NOx
Air
Air dryer
Flow meter
Ozone generator
Phase sensing freq.
Diff amp
NO2
Phase sensing freq.
Decay
Flow meter
NO cell
Photo-multiplier tube
Signal
Phase-sensitive amplifier
NO
NO
Flow constrictors

Figure 3.1. Oxides of nitrogen chemiluminescent analyzer

3.3.1.3.3.1 Tentative method for the calibration of nitric oxide, Nitrogen Dioxide and Ozone analyzers by gas phase titration--This technique developed by EPA for calibration of chemiluminescent oxides of nitrogen and ozone analyzers is a milestone in ambient air quality measurement. Reported in the Environmental Protection Technology Series, March 1974 (EPA-R2-75 246), its application substantially improves rapid calibration ability in the field. Integrity of the technique can be affirmed in the laboratory by certification using NO_2 primary standard permeation tubes.

The gas phase titration (GPT) technique uses the rapid gas phase reaction between nitric oxide and ozone so that with concentration of one of the three gases known, the concentration of the other two may be determined. Cylinder nitric oxide at 50 to 100 ppm in nitrogen is used as a secondary standard for routine field calibrations. Ozone is added to excess nitric oxide in the dynamic calibration system, and a chemiluminescent nitric oxide monitor indicates changes in concentration. The decrease observed on the spanned nitric oxide analyzer with addition of ozone is equivalent to the concentration of nitric oxide consumed, the concentration of ozone added and the nitrogen dioxide concentration produced. The advantages of the procedure are that a primary standard for only one gas is required and that rapid and routine calibrations of ozone, nitric oxide and nitrogen dioxide monitors may be performed at a common manifold as shown in Figure 3.2.

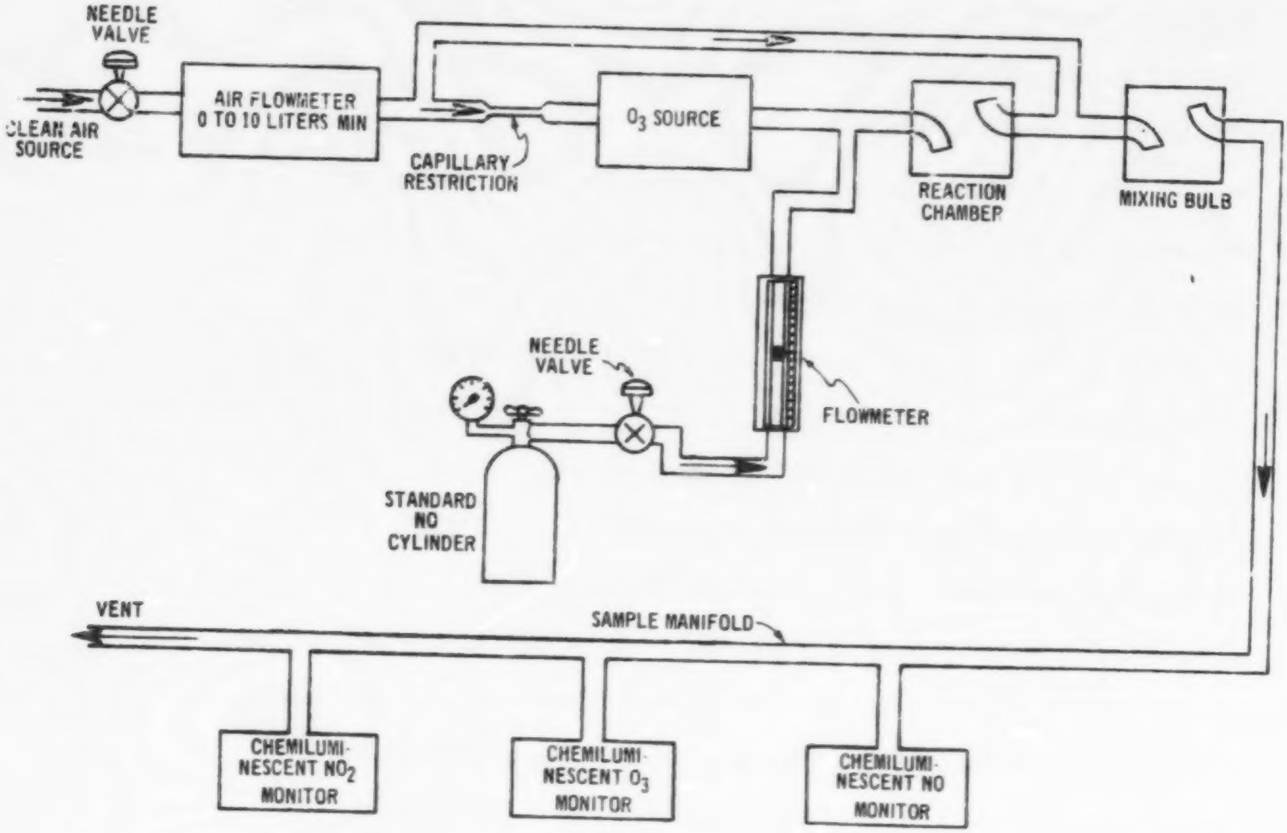

NEEDLE VALVE
CLEAN AIR SOURCE
AIR FLOWMETER 0 TO 10 LITERS MIN
CAPILLARY RESTRICTION
O3 SOURCE
REACTION CHAMBER
MIXING BULB
NEEDLE VALVE
FLOWMETER
STANDARD NO CYLINDER
VENT
SAMPLE MANIFOLD
CHEMILUMINESCENT NO2 MONITOR
CHEMILUMINESCENT O3 MONITOR
CHEMILUMINESCENT NO MONITOR

Figure 3.2. Flow scheme for calibration of NO, NO_2, and NO_x and O_3 monitors by gas phase titration

3.3.1.3.3 Electrochemical NO and NO_2 analyzer--Energetics Science, Inc. has produced a fully protable analyzer to measure NO and NO_2 separately and simultaneously.

The detection principle used is an advanced electrochemical method whereby NO is measured by oxidation and NO_2 is measured by reduction. The analyzer has dual ranges for both NO and NO_2 with the high sensitivity range for NO_2 being 0-1.0 ppm and for NO, 0-10 ppm full scale.

Prototypes with a full-scale sensitivity of 0.5 ppm are being engineered. Limitations include pronounced temperature sensitivity; the principal advantage of the analyzer is that it is portable and can be operated with a minimum of training.

3.3.1.3.4 NO$_2$ Fluorescence monitor--A laser-induced fluorescence monitor for NO$_2$ has been developed for EPA. A recent 30-day field study in St. Louis, Mo. comparing the fluorescent and chemiluminescent methods for NO$_2$ showed almost no difference between the two procedures. EPA is working on a system to induce NO$_2$ fluorescence with a pulsed high energy broad bank xeon source. Such a system would be simpler to operate and considerably less expensive than the laser method.

3.3.1.3.5 Nitrates--An automated instrument for nitrates has been developed. The system couples a wet microelectrostatic precipitator (Leap sampler) with a nitrate ion selective electrode. The solution from the Leap sampler is automatically pumped into a cell containing the ion selective electrode where the nitrate ion concentration is measured. The system is capable of measuring 1 $\mu g/m^3$ of NO$_3$ for a one-hour collection period. EPA is conducting field and laboratory tests on interferences and general performance characteristics.

3.3.2 Stationary Sources

The prescribed reference method for NO$_x$ uses the EPA sample train to collect a sample from the stack source and the phenoldisulfonic acid method for analysis.[1,2] The method is time-consuming (with respect to sample analysis) and needs improvement to increase reproducibility. Regulations allow for equivalent and alternative methods, but criteria and procedures for determining equivalency and acceptable alternative methods have not yet been proposed.

Guidelines have been developed for continuous NO_x monitoring systems and performance specifications proposed based on evaluation of commercially available systems.[3,4,5] Commercial systems are available using various sampling and analytical techniques. Both extractive and in-situ techniques are available. Analytical methods include: electronchemical, coulometric, UV, IR and visible absorption spectroscopy, colorimetric and chemiluminescent.

The reference method procedure is being evaluated to improve its reproducibility, minimize executive time and delineate critical performance parameters to be used as criteria for equivalent and alternative methods.

The lead dioxide method for NO_x developed on contract[6] is being evaluated as an alternative reference method for power plant emissions and will be evaluated also for application to other NO_x sources.

Evaluation studies have been done comparing various sampling approaches to continuous monitoring of NO_x emissions, namely, extractive, in-situ and remote sensing. A report on these studies is under way. A study has been completed on delineation and evaluation of criterical design and performance parameters of interface systems required in the use of extractive monitoring systems.[7] The study considered various pollutant gases including NO_x. An in-situ gas filter correlation NO_x monitor has been developed as a field prototype and is undergoing field evaluation.[8] Contract effort has been started to evaluate the application of the same technique to remote sensing of NO_x by IR emission compared with IR absorption in the in-situ device.[9] An inexpensive, simple NO_x monitor is being developed in-house.

Within a year or two enough data will be available to allow reassessment of research and development activities. At this time no additional activities are advised beyond completion of ongoing tasks and two tasks in future plans. One is development and evaluation of a myoglobin method as an alternative method for NO; the other is the evaluation of conversion efficiency of NO_2 in the chemiluminescent method for NO_x monitoring as applied to nitric acid plants.

3.3.3 Mobile Sources

Standards and techniques of measurement for nitrogen oxides have been promulgated for most mobile sources. These methods and technique result from research and development efforts of the Chemistry and Physics Laboratory. The analytical system specified throughout was the chemiluminescent nitric oxide plus ozone reaction with prior conversion of nitrogen dioxide to nitric oxide. Standardization and efficiency determinations are also made with CPL-developed procedures.

3.4 CARBON MONOXIDE MEASUREMENT

3.4.1 Ambient Air

Carbon monoxide (CO) is by far the largest single pollutant found in urban atmospheres. Although the background level is about 0.01 ppm, concentrations of 300 ppm have been reported in congested industrialized urban areas during prolonged periods of air stagnation.

CO is a product of incomplete combustion of carbonaceous fuels. The largest man-made source comes from the combustion of motor vehicle fuels. Estimates vary, but CO introduced into the atmosphere in the United States is from one-half to three-fifths of the global input, calculated to be about 2.25×10^{11} kg (250 million tons) annually. Without removal processes this input would be sufficient to raise the background 0.03 ppm per year. The mean residence time has been estimated to be between 0.2 and three years.

3.4.1.1 Calibration--Calibration of methods to measure carbon monoxide has probably been the hardest problem faced by the analyst. Probably it also accounts for measurements discrepancies and arguments that have arisen from comparing data. When there are problems in calibration, usually they can be traced to errors in concentration values of calibration gas sources or differences in the diluent gas. In many instances, these gases have a CO content higher than the ambient concentration the analyst has attempted to measure.

It appears that lacking a primary standard, manufacturers have assayed the concentration of a carefully blended mixture in a reference cylinder. This cylinder subsequently has been used to calibrate instrumentation to determine the content of subsequent mixtures blended to approximate the concentration requested. The reference cylinder might be used for many months, and during that period of time, the CO concentration is changing. Depending on the concentration of CO in the cylinder, the diluent gas and metallurgical aspects of the cylinder, the decay rate ranges from dramatic to tolerable. Some vendors periodically reassay the reference cylinder or prepare new mixtures to minimize the problem. Meanwhile, the cylinder concentration in the "certified" mixture is shipped to the consumer and change in the mixture occurs. If the CO concentration is very low, the cylinder wall oxidized or reactive impurities present, the CO level will decrease significantly within the first month before tapering off. The purchaser may use this "standard" cylinder for several years. It is not surprising, therefore, if standard cylinders are brought together from various sources and introduced into a single analyzer, that a difference of 7 ppm between cylinders certified at 25 ppm might be seen.

Aluminum cylinders for pressurized specialty gases introduced within the last year promise to substantially reduce the calibration problems of CO methods. The original assay of the mixture must be accurate, and this can only be accomplished now by rigorous attention to detail and use of expensive and delicate equipment by a very competent analyst. The purchase of such blends would be very expensive.

EPA is supporting investigation of generating precisely known concentrations of CO according to the scheme:

$$A \rightarrow B + CO,$$

where A is a compound capable of unimolecular decomposition (e.g., by pyrolysis) to produce a stoichiometric quantity of CO, and further being stable and volatile enough to be precisely dispensed from a permeation device. Metal carbonyls are excluded from consideration because of toxicity. Support is also being given to improvements in permeation/diffusion devices expected to facilitate the technique for dispensing precise small quantities of CO.

3.4.1.2 Manual Measurements--No new manual methods have become popular in the last five years. There may have been laboratory work on new manual techniques for ambient air analysis, but it has not been documented in air pollution literature.

3.4.1.2.1 American Public Health Association (APHA) Method--About two years ago the Intersociety Committee adopted the method for colorimetric determination of CO that uses a solution of the silver salt of p-sulfaminobenzoic acid. The solution is made by adding to 20 ml of p-sulfaminobenzoic acid, 20 ml of 0.1 M $AgNo_3$ and 10 ml of 1.0 M HaOH with shaking. Ten ml of the solution is transferred to a 125 ml Erlenmeyer flask with a standard taper joint at the mouth. A stopcock adapter is placed into this joint and the assembly is evacuated until the solution begins to bubble, after which the stopcock is closed and the assembly is removed. The sample is introduced simply by opening the stopcock. Total volume of flask plus stopcock adapter is determined by measuring the water required to fill the apparatus.

After introduction of the sample, the stopcock is again closed and the flask allowed to shake on a wrist shaker for two hours. A portion of the solution is transferred to a 1 cm spectrophotometer cell and the absorbance is determined at 425 nm for 0-400 ppm samples. The absorption at this wavelength results from the formation of a colloidal suspension of silver produced when the silver salt is reduced by CO.

Acetylene, olefins, H_2S and aldehydes in high concentration will interfere with this method either by reducing the silver or by formation of insoluble silver sulfide. These interferences can be removed by passing the sample through a silica gel filter containing $HgSO_4$. When standard samples are analyzed with each series of unknowns, replicate analyses agree to within ± 5%. Because this method is empirical, it is important that all conditions be maintained for the analysis of samples and standards. These include shaking time, the interval of time between completion of shaking and measurement and the temperature.

A long (two hours) shaking period is required because the reaction rate is slow and shaking increases the contact between reagent and gas sample.

3.4.1.2.2 Dräegor Type Tubes--There has been marked improvement in the last year or two in lower detection limits for devices manufactured by several firms based on the adsorption of CO on solid surfaces with a simultaneous color reaction. The method employs a hand pump which sucks air through a specially designed glass test tube containing the reagent. Depending on the kind of tube, the length of stain is either a measure of CO concentration in the tested air or a colorimetric comparison between standards and sample. Formerly these Dräeger-type tubes were considered a semi-quantitative means for rapidly detecting dangerous CO concentration in an industrial environment. Now, with care, concentrations as low as 2 ppm can be estimated with the length of stain tubes. The tubes are sealed and just prior to use, the glass tips are broken off the tubing ends, with the designated end coupled to the pump. The tubes are not reuseable. While it is not appropriate to use this technique to obtain a mean concentration (e.g., hourly average), it is useful for determining the approximate CO in an indoor/outdoor surrounding, a vehicle or other type enclosure.

3.4.1.3 Automated Analysis--A number of instrumental methods for automated analysis of ambient CO concentration are very satisfactory. Several instrumental methods that have been marketed have not been suitable, including amperometric, mercury vapor and certain species of electrochemical analyzers.

3.4.1.3.1 NDIR--The most popular technique used in commercial instrumentation for CO monitoring is the nondispersive infrared (NDIR) technique. This is also the basis for the reference method specified by EPA in Federal Register 36 (228) 22384, 1971.

NDIR analysis is based on broad-band spectral absorption sensitized for CO by means of a selective detector and optical filters. Commercial instruments for ambient CO concentrations are available from about four or five manufacturers in the U.S. and about the same number abroad.

Typical nondispersive infrared analyzers use a double-beam arrangement of the type shown in Figure 3. Infrared radiation from the filaments is directed onto two cells: (1) a reference cell filled with a non-infrared absorbing gas, such as nitrogen or argon, and (2) a sample cell through which the sample air containing the gas of interest is continuously drawn. The detector consists of a gas-impermeable double chamber with a flexible metal diaphragm as a partition. Both chambers are filled with the gas of interest. The infrared radiation passing through the reference cell enters one chamber of the detector, and radiation passing through the sample cell enters the other chamber. The gas in each chamber is heated by incoming energy, causing a pressure increase in the two chambers. The pressure rise is greater in the chamber receiving radiation from the reference cell, since a portion of the radiation transmitted through the sample cell has been absorbed by the gas of interest before entering the chamber on the sample cell side. This difference causes a diaphragm displacement which is electronically measured as a capacitance change. The infrared radiation is chopped by an optical chopper to cause a periodic capacitance change, which modulates a radiofrequency signal from an oscillator. The signal is subsequently demodulated, amplified, and the output fed to a meter or a recorder.

NDIR instruments are usually subject to interference because other gases (e.g., H_2O and CO_2) absorb at the wavelengths of CO. To eliminate or minimize interference, auxiliary absorption cells or optical filters are incorporated to remove most radiation at wavelengths at which the interfering substances absorb. This could be achieved, for example, by placing cells containing CO_2 in both light beams pictured in Figure 3.

For monitoring CO in ambient air, water vapor is the main interfering substance. Even using corrective filters, the discrimination ratio may be as much as 4000-7000:1 (i.e., 4000-7000 ppm of water vapor causes the meter to respond as if there were 1 ppm of CO). This could result in an error of as much as +5 ppm under humid conditions, although +3 ppm is more typical. Use of refrigerated dehumidification or drying traps reduces error to <1 ppm. Other sources of error include gas leaks in detector and reference cells, nonlinear response and drift in the electronic circuits. However, if conditions are optimum most analyzers set to span at 50 ppm full scale will reproduce to ±0.5.

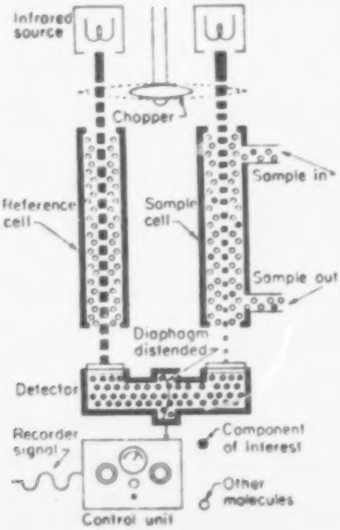

Infrared source
Chopper
Sample in
Reference cell
Sample cell
Sample out
Diaphagm distended
Detector
Recorder signal
Component of interest
Other molecules
Control unit

Figure 3.3. NDIR analyzer

3.4.1.3.2 Catalytic Oxidation--Detection of CO by catalytic oxidation has been reported in the literature over the years and analyzers incorporating the principle have been marketed. In the past, full-scale sensitivity has been about 0-500 ppm.

Within the last two years Mine Safety Appliances, Inc. (MSA) has converted CO to CO_2 by a catalyst called Hopcalite, and temperature increases as a result of the oxidation proportional to the CO concentration. Present MSA analyzers are measuring 0-10 ppm full scale reliably with drift tolerances for zero and span about ±1% per day. Shortcomings of this type instrument such as sensitivity to interferences have been practically eliminated in MSA's most recent design. The cost of the analyzer is competitive with NDIR analyzers. The same sensitivity can be achieved using gas chromatography techniques, but this analyzer is continuous and provides a real time analog signal. Unknown is how well the instrument will perform over a period of years.

3.4.1.3.3 Gas Chromatography--Gas chromatographic (GC) analyzers encompassing the automated measurement of CO have passed from the prototype stage to commercial production. Several hundred GC analyzers have been sold in the U.S. by a half-dozen manufacturers. Twenty-five St. Louis RAMS stations are equipped with the Beckman model 6800 which is designed to measure total hydrocarbons, methane and carbon monoxide.

The first automated GC analyzer for analysis of methane and carbon monoxide was developed by EPA. Commercial systems essentially are copies of the original design except for augmented analytical capability to include total hydrocarbons and in some cases other hydrocarbon species such as ethylene and acetylene. The basic system has an electronic program to cause the introduction of two sample aliquots. One is analyzed for its total hydrocarbon content by direct introduction into a flame ionization detector. The second aliquot is first transferred through a stripper column via a carrier gas. CO_2, water and all unwanted species of hydrocarbons are removed by the stripper column before it is backflushed for the next analysis. The eluting hydrocarbons and CO pass through a molecular sieve column, where the substances are separated, and through a catalytic reactor to a flame ionization detector (FID). The hydrocarbons pass through the catalytic reactor quantitatively and the CO is quantitatively converted to methane which is then measured by the FID.

The system is designed for semi-continuous operation and can perform an analysis about every five minutes. It has a linear output for measured substances and a wide operating range that suggests its use both in heavily polluted areas and relatively clean locations. Concentration of CO from about 0.03 pm to several hundred ppm can be measured with this instrument. The major disadvantage of this analyzer is that its complexity requires a highly trained, skilled operator. Data is not available for from several hours to several days following installation while the system stabilizes.

3.4.1.3.4 Dual Isotope Fluorescence--Modification of the NDIR method has been made using the principle of dual isotope fluorescence (DIF). The technique consists of absorption spectroscopy in which the source of energy is fluorescence of CO. This gives excellent wavelength correlation, high signal-to-noise ratio and discrimination. The system is illustrated in Figure 3.4. Infrared radiation from the Broadband IR source stimulates the CO molecules in the sealed fluorescent cell that in turn provide fluorescent radiation as the source of energy for absorption measurement. The chopper cells containing $C^{16}O$ and $C^{18}O$ are part of the analytical scheme whereby the measurement is uniquely sensitive to the presence of CO in the sample tube. If the $C^{16}O$ and $C^{18}O$ signals are defined as the "A" and "B" signals, respectively, only the "A" signal will be attenuated by the presence of CO gas in the sample tube since the natural isotopic abundance of $C^{18}O$ is only 0.2% of $C^{16}O$. The processing electronics generate an output proportional to the quantity:

$$\frac{B-A}{B}$$

This expression shows sensitivity to differential absorption of the two signals. In addition, maintenance of the "B" signal at fixed amplitude by automatic gain control allows the measurement to be independent of variations in source power of detector response.

Relatively high cost and a reported high incidence of malfunction and temperature sensitivity have held down widespread acceptance of the analyzer, but the latter two problems are being overcome. The license to manufacture the analyzer was purchased about a year ago by Beckman Instruments, Inc. for Andros, Inc.

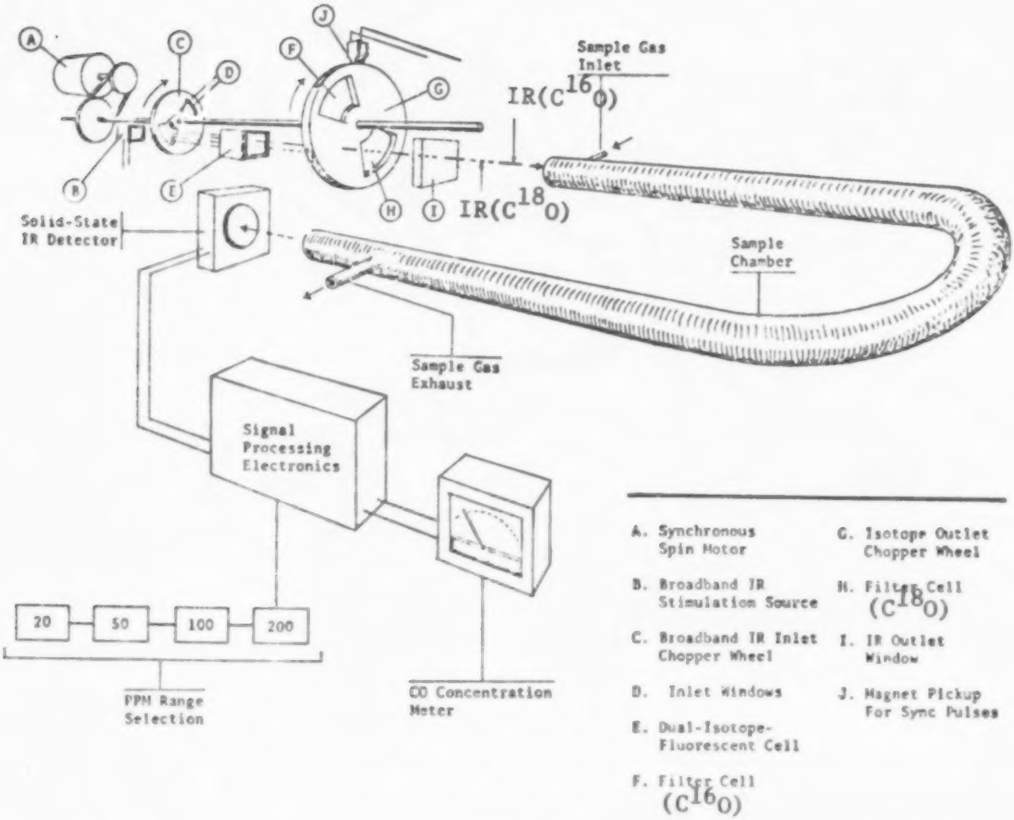

A
B
C
D
E
F
G
H
I
J
Sample Gas Inlet
IR(C16O)
IR(C18O)
Solid-State IR Detector
Sample Chamber
Sample Gas Exhaust
Signal Processing Electronics
20
50
100
200
PPM Range Selection
CO Concentration Meter
A. Synchronous Spin Motor
B. Broadband IR Stimulation Source
C. Broadband IR Inlet Chopper Wheel
D. Inlet Windows
E. Dual-Isotope-Fluorescent Cell
F. Filter Cell (C16O)
G. Isotope Outlet Chopper Wheel
H. Filter Cell (C18O)
I. IR Outlet Window
J. Magnet Pickup For Sync Pulses

Figure 3.4. Dual isotope fluorescence analyzer

3.4.1.3.5 Electrochemical Analyzer--At the time of this writing, Energetics Science, Inc. (ESI) had sold about 2500 "Ecolyzers," with the number sold now over 100 per month. In the future it could be the most prevalent instrument in the U.S. for ambient CO analysis. Because of the Ecolyzer's importance, we are quoting the entire conclusion of an EPA, ERC, Environmental Monitoring and Support Laboratory manuscript presented at the Instrument Society of America Symposium, May 13-15, 1974:

> "ESI has made available to the air pollution analyst a low cost useful instrument. The analyst must be alert to the analyzer's limitations. He should keep them in mind in using the analyzer

> and exercise caution in assessing the values obtained in terms of absolute accuracy.
>
> We view the Ecolyzer as a portable analyzer that gives us a capability for rapidly sighting potential or real dangers be it in a garage, tunnel, intersection, industrial plant or inside a conveyance. It is an analyzer that is suited for that type of emergency episodes where one need not be as concerned about accuracy as about the concentration in terms of a hazardous situation. Portability of the analyzer makes it useful for locating a "hot spot," a place where higher concentrations occur and if interest lies in that direction, locate a permanent sampling site. The Ecolyzer should be kept in a condition of readiness for the activities mentioned above. A weekly check of its operational condition and calibration would be in order. A spare sensor on hand would likely be desirable.
>
> The Ecolyzer is not looked upon as desirable for continuous operation at a fixed monitoring site. Problems of linearity, drift, temperature sensitivity, rise vs. fall time are potential sources of error that could prove misleading.
>
> A person with little training can take an operating instrument into the field and obtain satisfactory results.'

The calibrated pumps a constant flow of sample air through a filter and sensor. Carbon monoxide in the sample air is electro-oxidized to carbon dioxide (CO_2) at a catalytically active electrode in an electrolyte as shown in the reaction: $CO + H_2O \rightarrow CO_2 + 2H^+ + 2e$.

The electro-oxidation of CO occurs at a sensing electrode in a sulfuric acid electrolyte. The counter electrode is the cathode where oxygen reduction occurs. Additionally, a reference electrode is necessary for operation of a potentiostat to balance the system. In the electro-oxidizing reaction, current flow between sensing and counter electrodes is approximately proportional to the CO concentration of the sample and is registered on a meter or an optional recorder.

3.4.2 Stationary Sources

A large number of commercial CO analyzers are available including manual methods (colorimetric) and instrumental methods (catalytic oxidation, electro-chemical cell, gas chromotograph--flame ionization, NDIR and DIR). Gas-filter correlation (GFC) is an advanced form of NDIR which has all but eliminated the interference from water vapor, CO_2 and particulates. By combining GFC with an in-situ, or non-extractive cross-stack measurement, a continuous, accurate CO measurement can be made without problems of sample extraction and handling. One instrument using this method is commercially available, and a second is expected to be on the market in early 1975. The GFC technique is also applicable to remote, single-ended measurement of CO emissions.

3.5 HYDROCARBONS

3.5.1 Ambient Air

Biological processes, petroleum, coal and natural gas account for almost the total hydrocarbon loading of the atmosphere.

Complex problems are involved in study of the reactants and products of atmospheric photochemical reactions, one being the determination of atmospheric hydrocarbon levels and their relation to hydrocarbon emission from vehicles and other sources. The greatest interest is in those hydrocarbons participating in photochemical reactions.

While methane is innocuous and does not participate in photoinitiated reactions, it does constitute a major portion of hydrocarbons present in the air, and in certain areas and atmospheric conditions has accounted for more than 95% of hydrocarbons present. Typically CH_4 makes up nearly all the nonreactive fraction.

Thus a rough correlation exists between "reactive hydrocarbons" and "total hydrocarbons less methane." Pending development of a type-specific method for determining reactive hydrocarbons, a compound specific method has been found to be useful and is now used in setting national primary and secondary ambient air quality standards for hydrocarbons.

The standard as written does not allow for natural sources of hydrocarbons such as the terpenes, which emit into the global atmosphere an estimated 1.8×10^{11} kg/yr. The terpenes are associated with forest areas and the blue haze of the Appalachian Mountain region. Concentrations of total hydrocarbons less methane have been found in remote rural surroundings at levels close to the standard. The participation of naturally occurring hydrocarbons in photochemical reactions producing oxidants is under investigation.

There are limitations to the categorization of all hydrocarbons of other-than-methane species into a single grouping. Given the same conditions for photoreaction, half-life for some hydrocarbons will be minutes while for others it will be hours to days. It is known that the reactivity (make-up) of the grouping may differ markedly from one urban area to another. For example, gas chromatographic analysis has shown that within the same urban area (the Los Angeles basin), make-up of the grouping is such that relative reactivity (near the Pacific coast in the morning) is notably greater than the same carbon concentration of the same air parcel reaching another portion of the city later in the day (inland Azusa area).

3.5.1.1 Calibration--Blends of CH_4 in air, pressurized in gas cylinders, have been used over the years for field calibration of HC analyzers. The mixture even at low concentration is stable for long time periods. Capability was developed as early as 1965 for preparing concentrations in the ppm region with a tolerance of ±0.1 ppm. Although demanding and time-consuming, the technique gave EPA an ability to evaluate the product of commercial suppliers. Until several years ago, cylinders delivered by manufacturers had a certified analysis either moderately or grossly inaccurate, although there was one reliable gas supplier. Recognizing a need, competitors have now upgraded their products so that accurate standards of low molecular weight hydrocarbons are available from a number of them. In the laboratory and for special studies, mixtures of hydrocarbons, including the reactive species, can be made by skilled personnel in inert plastic bags or chambers for specialized studies or calibration of special analytical methods. Included are gas chromatographs and sophisticated 1R, VV and fluorescent analyzers. This in-house capability has helped EPA study atmospheric kinetics and photochemical reactions.

Presently the agency has the problem of an acceptable hydrocarbon to calibrate analyzers measuring the fraction of other-than-methane hydrocarbons in the atmosphere.

Very accurate concentrations of one or more hydrocarbons can be delivered using the EPA permeation technology. At least a score of permeation tubes containing different species of hydrocarbons have been successfully fabricated and used for this purpose. Many are commercially available.

3.5.1.2 Manual Methods--Improved collection media for hydrocarbons has been the object of several investigations in recent years. Subsequent stripping of the hydrocarbons for indentification by mass spectrometry or quantification by gas chromatography has helped the laboratory researcher in profiling more than two hundred hydrocarbons found in polluted atmospheres.

No new wet chemical methods of significance have surfaced in the last seven or eight years. In Air Pollution, Vol. II, ed. Stern, A. C. P. 15 Academic Press, 1968, Altshuller described manual methods for measuring certain hydrocarbon species or groups.

3.5.1.3 Automated Analysis--As stated earlier, EPA's interest in hydrocarbon measurement is primarily related to reactive hydrocarbons grouped into a category referred to as hydrocarbons corrected for methane, which is in turn called hydrocarbons as methane (i.e., total count of carbon atoms, C, in the measured sample) minus the methane, CH_4, concentration. Conventional instrumental systems measure total hydrocarbon concentration and methane separately.

The Federal Register, 36 (158) 15491, August 14, 1971 states "it may be assumed that the degree of total hydrocarbon emission reduction necessary for the attainment and maintenance of national standard for photochemical oxidants will also be adequate for the attainment of the national standards for hydrocarbons." EPA therefore does not require states to monitor hydrocarbons for compliance with national ambient air standards.

In 1974 an EPA investigation found a lack of comparability between different commercial analyzers for non-methane hydrocarbon. Reasons for the discrepancies are still being investigated.

3.5.1.3.1 Gas Chromatography--A procedure for collection and concentration of trace hydrocarbons and rigidly controlled introduction into a GC where separation of compounds takes place and compounds elute into a flame ionization detector. Compounds generally elute in relation to their mass, with heaviest species last on the chromatogram. The peaks have qualitative and quantitative meaning gained by systematic empirical fingerprinting through analysis of measured concentrations of known hydrocarbons. Advances in chromatography have allowed speed-up of the analysis by temperature programming automatic peak identification and quantification using state-of-the-art magnetic tape recorders with sophisticated peak identification and integration (concentration) printout systems.

3.5.1.3.2 Programmed Gas Chromatograph--The reference method for determination of hydrocarbons corrected for methane is contained in Federal Register, 36 (84), April 30, 1971, as described earlier. This reference method is being reevaluated. Present commercially available instruments using the technique are expensive, complex and demand considerable operator skill. They are marginal in ability to measure hydrocarbons corrected for methane on a routine unattended basis at or below levels required by the national ambient air standard.

3.5.1.3.3 Reactive Hydrocarbon Analyzer--Bendix Process Instruments Division has made available its model 8201 Ambient Hydrocarbon Analyzer designed to measure what Bendix calls "reactive" hydrocarbons (total hydrocarbons less CH_4). In operation, a programmer causes an aliquot of sample air to be transported through a column via a carrier gas. Hydrocarbons other than CH_4 are stripped from the gas stream in the column. Following the elution of CH_4, the column is back-flushed, and the CH_4 is carried to a FID for measurement, amplification and signal storage. Then a discrete volume of ambient air is passed directly to the detector for measuring total hydrocarbons; the signal is also amplified and stored. The concentration of CH_4 is then electronically subtracted from total hydrocarbon concentration for the measurement of "reactive" hydrocarbons. During each programmed cycle, approximately three minutes long, automatic zeroing of the detector output ensures a stable base line.

When first evaluated this analyzer had several weaknesses that were almost eliminated by substitution of more rugged components and plumbing changes. Currently there are about 300 such units in the field.

3.5.1.3.4 Dual Channel Hydrocarbon Analyzer--The Mine Safety Appliances Company (MSA) instrument is nearly a complete system in itself, and is a recent commercial development in hydrocarbon instrumentation. The device is independent of programming, mechanical and electromechanical functions and has a built-in supply of zero gas and purified combustion air. All that must be supplied is hydrogen and electrical power. (See Figure 3.5.) Operation entails continuous measurement of two gas streams: one stream containing only CH_4, the other THC. The two streams are simultaneously introduced into a dual flame detector mounted in a constant-temperature-controlled oven. The CH_4 stream is ambient air passed through a catalyst column containing Hopcalite (TM) at 260°C. Essentially all hydrocarbons except CH_4 are converted to carbon dioxide (CO) and water vapor, and all CH_4 is passed to the detector. The instrument, designated 11-2 by MSA, has a built-in pump and catalytic oxidizer supplying purified combustion air and is used as a source of zero air for calibration of the analyzer. The electronic design provides for continuous voltage generation proportional to the total hydrocarbon, CH_4 and nonmethane concentrations. (See Figure 3.6.) Both sides of the system are calibrated using a known concentration of CH_4 in air; range selectors plus manually adjusted potentiometers permit exact alignment so that hydrocarbon other than CH_4 will be accurately reflected as nonmethane.

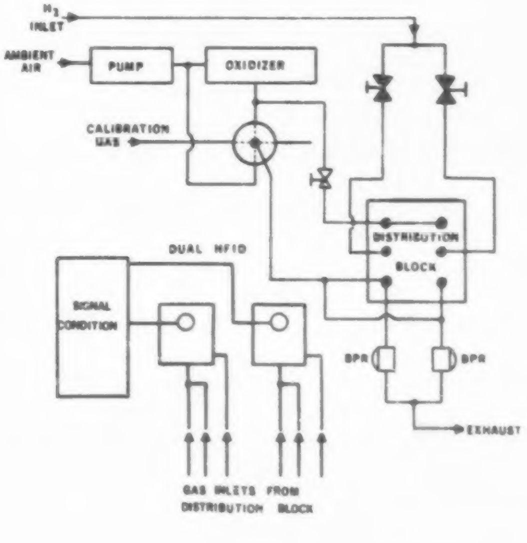

H_2 INLET
AMBIENT AIR
PUMP
OXIDIZER
CALIBRATION GAS
DISTRIBUTION BLOCK
DUAL HFID
SIGNAL CONDITION
BPR
BPR
EXHAUST
GAS INLETS FROM DISTRIBUTION BLOCK

Figure 3.5. Block diagram of dual hydrogen flame detector

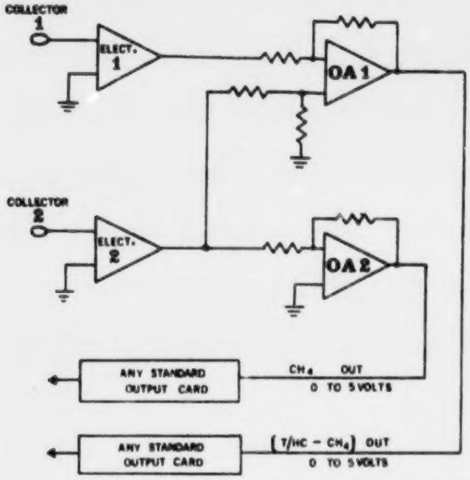

COLLECTOR 1
ELECT. 1
OA 1
COLLECTOR 2
ELECT. 2
OA 2
ANY STANDARD OUTPUT CARD
CH_4 OUT
0 TO 5 VOLTS
ANY STANDARD OUTPUT CARD
$(T/HC - CH_4)$ OUT
0 TO 5 VOLTS

Figure 3.6. Electronic diagram of dual flame detector

3.5.1.3.5 Chemiluminescence--A new technique has been developed by EPA which reacts hydrocarbons in air with atomic nitrogen to produce a chemiluminescence approximately proportional to the photochemical reactivity of hydrocarbons present in the air sample. The method has applicability for measuring reactive hydrocarbons species in auto exhaust as well as for measuring the photochemical potential of air samples containing hydrocarbons.

Another detector developed by EPA is based on the reaction of olefinic organics with an excess of ozone. The method is analogous to the ozone, ethylene reaction currently used to monitor ambient ozone except that the roles of ozone and ethylene (olefinic organic) are reversed. The method gives either a single measure of reactivity or, with a gas chromatographic column, can monitor individual hydrocarbons.

3.5.2 Stationary Sources

Ambient air quality standards for hydrocarbons relate the photochemical reactivity of these species to oxidant formation so that any future requirement on measurement of emissions from stationary sources must consider: (1) emissions which react mutually or in the presence of other atmospheric contaminants to produce oxidant, and (2) emissions which react photochemically and serve as precursors of oxidant formation.

The use of present analytical hydrocarbon measurement techniques applied to source emissions is limited. Both total hydrocarbon and non-methane hydrocarbon instrumentation used for ambient air measurement have been used, and there is a need for development of adequate sample interface systems. Monitoring systems based on process gas chromatography have been shown to be impractical, since separation schemes would have to be developed on a source-by-source basis. Manual or "compliance-type" methodology requires a sample collection scheme using bag collection, freeze-out traps, or charcoal adsorption devices for collecting samples in the field with laboratory analysis using gas chromatography.

At present, our research and development efforts involve a grab-sampling system which can collect emissions in class fractions, i.e., paraffins, olefins, aromatics, oxygenates and halogenated compounds. The class fractions can then be analyzed collectively in the laboratory by a total class hydrocarbon measurement or by on-column injection into a chromatograph for identification of each species within a class. The objective is to provide basic emission data from a variety of source emissions.

3.5.3 Mobile Sources

Procedures for measuring total pollutant hydrocarbons and conditions under which they are measured are defined in the Federal Register based on their ability to participate in oxidant forming reactions. Mobile sources thus regulated include light- and heavy-duty over the raced vehicles and aircraft. Oxidants per se are not emitted directly from motor vehicles, but formed later after photochemical reactions. Most hydrocarbons are capable of forming oxidants photochemically in the presence of NO_x; exceptions are methane, propane, acetylene and benzene. Other organic emissions such as oxygenates and nitrogen compounds may also participate while higher hydrocarbons including such classes as the polynuclear aromatics, i.e., benzo-a-pyrene, may not be reactive. These compounds may be either gases or particulates depending upon conditions, molecular weight, concentrations, etc.

Mobile sources are diverse, each requiring special measurement techniques. In all cases, mobile sources are considered diffuse sources, i.e., sources in which no individual is a significant contributor but the sum of all sources is of great importance. Mobile source emissions are directly related to conditions of operation as well as to other factors, such as environment and fuel.

Sample collection is critical to all sources and is of overriding importance with mobile sources. The constant volume sampler (CVS) has been specified in the regulations as the method used to integrate samples collected over a total operating cycle, allowing the total mass of pollutant emitted to be measured and mass weighed in relation to its impact. The procedure causes an average dilution of about 10 to 1. As applied to well-controlled vehicles, this extra diffusion increases the sensitivity requirements of the analytical system to levels approaching those of ambient air.

Dilution of the CVS stream provides cooling and time for particulate formation to occur. The cooling is especially important as temperature fluctuations of many hundred degrees occur. The CVS system as specified allows the cycle to be broken into three segments with each segment analyzed and weighed separately. Routine measurements for hydrocarbons are made on samples collected in bags, while more reactive materials such as oxygenates are collected directly from the gas stream.

The specified analytical system uses the Flame Ionization Detector (FID). This measures total carbon concentration in the flame and therefore allows an estimate of mass emissions to be made although mole concentrations are not defined. It is used in detailed gas chromatographic (GC) systems as well as in total hydrocarbon analyzers. The operation in the two systems is somewhat different, with the total FID operating as a premixed flame while the GC system operates as diffusion flames. This difference has important consequences when catalytically controlled vehicles are tested, since individual response factors for hydrocarbons are dependent on operating conditions. Methane is more refractory to catalytic composition than other materials and may be markedly enhanced in vehicles so equipped. Recent work, both in-house and by others, continues to show the importance of response factors and effects of operating conditions and oxygen content on them.

GC systems have been designed to routinely measure non-reactive components. Methane alone may be measured by simplified GC systems or directly by infrared gas correlation spectrometry. Standard infrared techniques are inhibited by water vapor interferences. A rejection ratio of 10^5 or greater is required.

Detailed hydrocarbons are determined by sophisticated GC methods. In this laboratory, 52 individual compounds are measured by an automated system programmed from -100°C to 75°C. The specificity necessary determines the type of separations made and other systems have been used.

Higher molecular weight hydrocarbons are determined by several methods. Usually other material is first trapped, isolated, on a short column containing appropriate packing material such as chromosorb 101 or firebrick and "tris." This precolumn or collection column becomes the first part of the analytical column. For diesel emissions the most common columns provide boiling point separations only, since there are too many isomers present to separate in a reasonable time. These techniques are also applicable to higher molecular weight substituted compounds such as oxygenates.

Use of liquid chromatography is becoming widespread for the separation of higher organics, and a system combining these techniques is used to evaluate diesel and jet odor.

Higher molecular weight materials are very susceptible to wall losses and reactions. All surfaces must be heated to prevent such losses and much earlier work must be doubted due to poor practice.

Oxygenates is a commonly found class of organics in emissions of all mobile sources. They are usually analyzed after derivative formation either by spectrophotometic or chromatographic procedures. Current methodology is not fully satisfactory because of interferences and difficulty in performing analysis. Spectrophotometric methods may be applicable to specific compounds such as formaldehyde.

Polynuclear aromatics analysis is not completely satisfactory at this time. Procedures are complicated and reproducibility and sensitivity are problems. Screening methods have been developed for specific members of this series, but even these are non-routine, the large number of compounds in the class further complicating analysis.

Other non-regulated organics are just now being sought. These involve compounds of nitrogen and sulfur.

3.6 PHOTOCHEMICAL OXIDANTS

3.6.1 Ambient Air

Photochemical oxidants (O_x) are a class of atmospheric pollutants arising from reactions between hydrocarbons and oxides of nitrogen in the presence of sunlight. The class is known primarily for ozone peroxyacyl nitrates--mostly peroxacetl nitrate (PAN)--and hydrogen peroxide. The latter two compounds in a highly oxidant atmosphere like Los Angeles may each represent 10% of the total (O_x) concentration, while in a reducing atmosphere like New York City, they each may account for 2% of the total. Their chemical formulas are:

ozone	O_3
peroxacetyl nitrate (PAN)	CH_3COONO_2
hydrogen peroxide	H_2O_2

Photochemical oxidants traditionally have been defined by air pollution agencies as atmospheric substances which will oxidize certain reagents, the most frequently used being a solution of neutral-phosphate-buffered potassium iodide (KI). This reagent responds to ozone, nitrogen dioxide and the peroxyacyl nitrates, and, to a lesser extent, to hydrogen peroxide. Reducing agents such as sulfur dioxide (SO_2) have the opposite effect of oxidants on the reagent solution. The KI method may be used, therefore, to provide a measure of net oxidizing properties of atmospheric pollutants without complete discrimination as to species of oxidants or reducing agents.

Various terms describe photochemical oxidant concentrations. Two of the terms, "oxidant" and "total oxidant," are used to describe the "net" oxidizing ability of the sampled air. Use of these non-specific terms is required because measurement (usually by the KI method) does not always differentiate between oxidizing or reducing agents. The terms "corrected oxidant" or "adjusted oxidant" show that the measurements have been corrected for certain known responses (usually SO_2 and NO_2) other than ozone or peroxyacetyl nitrate. The term "ozone" and "peroxyacetyl nitrate" show that the measurement method is specific for these gases.

We emphasize that the terms, "photochemical oxidant," "total oxidant," "oxidant," "corrected oxidant," and "adjusted oxidant," have no exact meaning since response obtained in the KI method depends on the presence of various substances responding in a different manner.

3 6.1.1 Calibration--Ozone generator calibration systems are available from nearly a dozen commercial suppliers. Generally they are quality products stable, reliable and able to be taken into the field. EPA was responsible for the basic design of the generators (Figure 3.7). The ozone source is an ultraviolet mercury lamp which irradiating a quartz tube through which clean air flows at 5-10 liters/minute. Ozone

concentrations from 0 to 1 ppm can be generated by varying UV intensity with a variable shield around the lamp envelope and the flow rate is controlled by a needle valve and measured by a rotameter. The ozonized air passes to a manifold from which the monitor under test draws its sample.

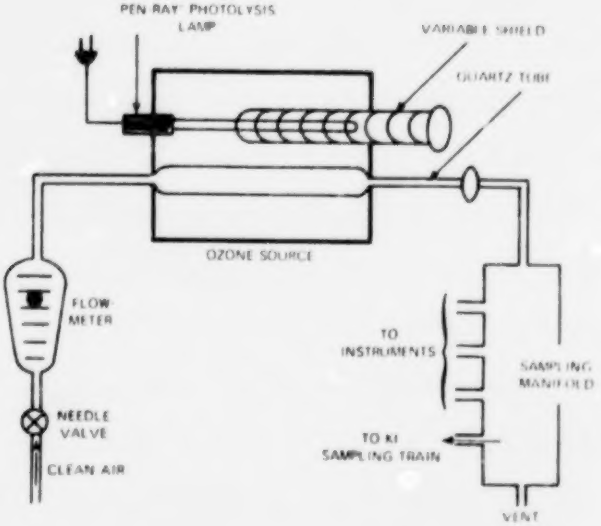

PEN RAY PHOTOLYSIS LAMP
VARIABLE SHIELD
QUARTZ TUBE
OZONE SOURCE
FLOW METER
NEEDLE VALVE
CLEAN AIR
TO INSTRUMENTS
SAMPLING MANIFOLD
TO KI SAMPLING TRAIN
VENT

Figure 3.7. Typical ozone source, dilution and manifold system

In using ozone generators, care must be taken to eliminate all impurities including NO in the diluent air stream.

Thus far only a source of ozone has been described. This source, which has a numerically indexed variable shield for precisely reproducing settings, must be calibrated using a primary calibration method. The presently accepted primary standard calibration method is the manual wet-chemical KI method described in Federal Register, 36 (84) 8196, April 30, 1971.

3.6.1.2 Manual Measurement--Methods used for the measurement of photochemical oxidants (O_x) range from those responsive to all oxidants and reductants (and therefore indicate to a degree a "net" oxidizing effect) to those which respond most to a specific oxidant such as O_3.

It is possible to apply corrections to a value obtained using a given manual method to improve accuracy. For example, using the (to-be-discussed) KI method one can correct for the positive interference of NO_2 and negative interference of SO_2 if concentrations of each are known. An ideal method for O_x does not exist and is not likely to be found. Such a method would have an equivalent response for all photochemical oxidants including O_3, PAN and other peroxyacyl nitrates, the aldehydes (formaldehyde and acrolein), peroxbenzoyl nitrate, H_2O_2, alkyl hydroperoxides, organic peroxide and as yet unidentified other compounds believed to account for certain measurement anomalies. The method would not respond to any atmospheric reductants such as SO_2, or oxidants not photochemically generated, such as most NO_2.

Compounds measured can differ dramatically in reactivity, and therefore the true measure of potential damage to man, other animals, vegetation and materials would be unknown. Further, some NO_2 present in polluted atmospheres is photolytically generated.

Fortunately the problem is not as formidable or perplexing as it seems. O_3 is at least the most abundant of the O_x compounds and ranks in the top group of reactive species, so that an accurate fix on O_3 concentration would provide a meaningful measure of harmful O_x in the polluted atmosphere.

3.6.1.2.1 Rubber Cracking--A quantitative method for determination of O_3 was developed by Haagen-Smit and Bradley in 1951, the essence of the procedure being to put a flat rubber strip under stress, bending it to form a tight "u" clipped together at the ends, placing it in a glass tube and drawing the raw atmosphere directly over it until cracking appeared at the outer edge as seen using a 3X eyepiece. The exposure period preceding the appearance of cracks served as an index of the O_3. We mention this procedure since high O_3 concentrations from the 1950's through '60's were reported by the Los Angeles County Air Pollution Control District (LAAPCD) using rubber cracking.

Variations have been investigated including microscopic measurement of crack depth, elongation of a weighted rubber strip and continuous unattended open exposure of a strip for a prolonged time with subsequent optical examinations to estimate total material effect. The original method required a skilled operator, was time-consuming and necessitated close scrutinty during analysis. The other procedures had shortcomings limiting their use to where error tolerances were not stringent.

3.6.1.2.2 Colorimetric Procedures--As with colorimetric procedures discussed earlier, optical absorbance of a solution is measured spectrophotometrically: the absorbance is linearly proportional to concentration of the colored species which ideally is directly proportional to the concentration of pollutant.

There are about eight proceduralized manual methods. Manual methods have various advantages and disadvantages, depending on the information desired, personnel available and other considerations.

Ambient manual oxidant sampling using wet chemistry depends on a collection device as illustrated in Figure 3.8. Sampling precautions are strict owing to reactivity of the pollutant. Sample systems should be fabricated preferably from glass or teflon. Location of the intake probe can be critical, and consultation with an expert is advised.

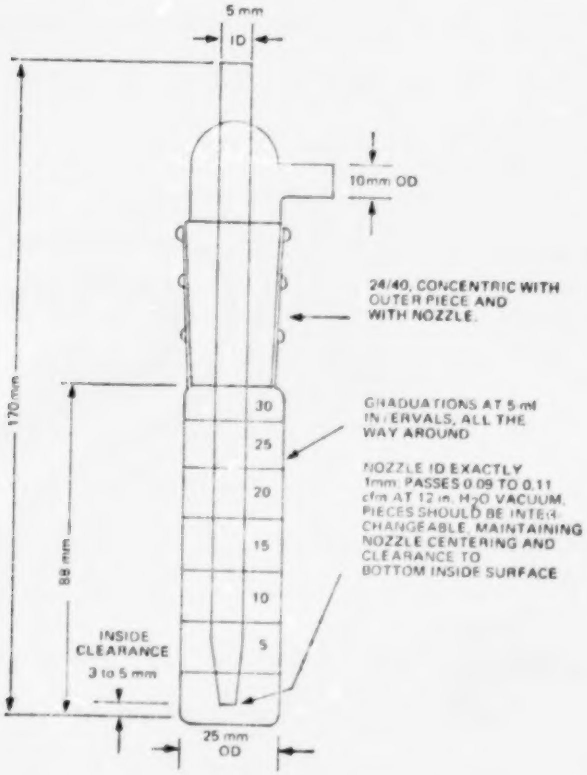

5 mm
ID
10mm OD
24/40, CONCENTRIC WITH OUTER PIECE AND WITH NOZZLE.
GRADUATIONS AT 5 ml INTERVALS, ALL THE WAY AROUND
NOZZLE ID EXACTLY 1mm; PASSES 0.09 TO 0.11 cfm AT 12 in. H_2O VACUUM. PIECES SHOULD BE INTERCHANGEABLE, MAINTAINING NOZZLE CENTERING AND CLEARANCE TO BOTTOM INSIDE SURFACE
30
25
20
15
10
5
170 mm
88 mm
INSIDE CLEARANCE
3 to 5 mm
25 mm OD

Figure 3.8. All-glass midget impinger

3.6.1.2.2.1 Neutral Buffered Potassium Iodide Method--This has been adopted as the tentative standard manual reference method by the Intersociety Committee and the ASTM Committee D-22 on Sampling and Analysis of Atmospheres and is also the EPA reference method for calibration of ozone generators.

In this method oxidants are absorbed in a one percent potassium iodide (KI) solution buffered at pH 6.8 ± 0.2. For ozone the reaction can be written:

$$O_3 + 3KI + H_2O \rightarrow K^+I_3^- + 2KOH + O_2$$

The liberated tri-iodide ion (I_3^-) is measured colorimetrically at 352 nm and is directly related to the concentration of ozone in the air sample. A 1:1 stoichiometry between moles of O_3 absorbed and moles of tri-iodid ion released is accepted. Sampling efficiency is very high when two impingers are used in series.

Oxidant measurement in a range from about 0.01 to 10 ppm is possible. SO_2 produces negative interference equivalent to 100% of an equilmolar concentration of O_3, but the interference can be removed with a U-tube containing an absorber located in the sampling train upstream from the impinger. The absorber usually is of glass fiber paper impregnated with chromium trioxide. Since the SO_2 absorber oxidizes any nitric oxide in the air sample to nitrogen dioxide, a correction for nitric oxide will be required. The chromium trioxide scrubber can, if wet, cause loss of O_3 and NO_2. NO_2 is known to give a response in one percent KI equivalent to 10% of that for an equimolar concentration of O_3. The contribution of NO_2 to the oxidant reading is eliminated by concurrently analyzing for NO_2 and subtracting one-tenth of the NO_2 concentration from total oxidant value.

PAN gives a response approximately equivalent to 50% of that of an equimolar concentration of O_3. Other oxidizing agents will cause positive interferences with this method. Other reducing agents, in addition to SO_2, can cause negative interference.

Color measurement is recommended within 30 to 60 minutes after sample collection. Time is required for color development (10-20 minutes), but color will fade with more than 60 minutes. Evidence is that the amount of tri-iodine ions liberated by O_3 depends on design of the gas bubbler and phosphate concentration of neutral pH. Error due to these variables is probably about plus or minus 10% of true value.

The neutral buffered KI procedure was the EPA reference method for determining oxidants until its replacement in 1971 by the continuous chemiluminescent method. The KI method remained in the primary dynamic calibration method for instrumental analysis methods.

3.6.1.2.2.2 Alkaline Potassium Iodide Method--This method is for manual determination of oxidants in the range of about 0.01 ppm-20 ppm. An absorbing reagent of potassium iodide in sodium hydroxide solution is used. After sampling the solution is treated with H_2O_2 to remove SO_2 interference and is finally acidified with phosphoric acid containing a small amount of sulfamic acid to release iodine for spectrophotometric measurement.

The advantage over the neutral-buffered potassium iodide method is that delay between sampling and completion of analysis does not involve color fading. This procedure requires a stoichiometric correction factor--0.65 mole of iodine is liberated for each mole of ozone absorbed. Rapid acidification is necessary because of certain irreversible losses of microquantities of iodine. The neutral-buffered KI method is preferred for its simplicity over the alkaline KI method.

3.6.1.2.2.3 Phenolphthalin Method--This method is based on oxidation of phenolphthalin to phenolphthalein. Phenolphthalein is pink in alkaline solution.

Because the technique is very sensitive to pH and temperature changes, it has dropped out of usage. Concentration measurements obtained by it are about twice those obtained by the neutral-buffered KI method so that it is necessary to correct data for the difference.

3.6.1.2.2.4 Other Manual Methods--Miscellaneous acceptable methods were developed in the late fifties and throughout the sixties, with EPA researchers responsible for the 1,2-di-(4-Pyridyl) ethylene method - (DPE) method, Ferrous Ammonium Sulfate method and Saltzman and Gilbert method based on the reaction of O_3 with NO to form NO_2 with wet chemical analysis for NO_2. Outside of EPA were the 4-allyl-2-methoxyphenol method - (Eugenol method, sodium diphenylamine sulfonate method and Acid Potassium Iodide method) - (Deutsch) method.

It is clear why some methods have not survived. The Ferrous Ammonium Sulfate method was used in EPA's National Air Sampling Network (NASN) for 24-hour sampling of total oxidant. Correlation between measurements by this method and those of the continuous colorimetric analyzer were poor and NASN discontinued its use. All methods used in the field lacked some desirable characteristic. Part of the problem may be lack of a clear-cut description of the substance to be measured; publication of the "equivalency document" to be discussed later should provide needed criteria.

3.6.1.3 Automated Analysis

3.6.1.3.1 Colorimetric Analyzers--Colorimetric continuous analysis of total oxidants almost always involves a 10 or 20% solution of neutral-buffered potassium iodide as the absorbing medium. The first instrumental approach in general use was the colorimetric oxidant recorder developed in 1953 by Littman and Benoliel. Instruments of this design using a 20% neutral-buffered KI solution were incorporated into the Los Angeles County Air Pollution Control District (LACAPCD) air monitoring station network in the early 1950's. About 1957 the KI was reduced to 10% because of objectionable crystal build-up. The instruments continue in use.

Sample air is passed at a known rate through a liquid absorbing reagent with a vacuum-pump arrangement. Oxidants in contact with the KI react to liberate the tri-iodine ion (I_3^-) which is determined spectrophotometrically at 352 nm and recorded on a strip chart recorder as ppm oxidant. Figure 3.9 illustrates a typical colorimetric analyzer. The reaction with ozone at pH 6.8 ± 0.2 is approximately:

$$O_3 + 3KI + H_3O \rightarrow K^+I_3^- + 2KOH + O_2$$

Colorimetric oxidant analyzers operate best at atmospheric oxidant levels ranging from 0.01-1.0 ppm of ozone or other equivalent oxidant.

SO_2 produces a negative interference equivalent to 100% of an equimolar concentration of oxidant. Response to NO_2 varies with the reagent formulation and scrubber design. For 10% KI, NO_2 produces positive interference of approximately 20%; for 20% KI, an interference of approximately 30%.

Filters and scrubbers for removing SO_2 have been used, but information as to performance is not available. One device often used consists of glass fiber strips impregnated with chromium trioxide (CrO_3) and sulfuric acid (H_2SO_4). As discussed in 3.6.2.2.1 (Neutral Buffered Potassium Iodide Method), these scrubbers convert a portion of the ambient NO to NO_2, necessitating an additional correction factor. Despite these drawbacks, CrO_3 scrubbers are the most generally used for removing SO_2 interference, and they are particularly useful during periods of high SO_2 concentration. (When SO_2 levels are less that 20% of the NO concentration, use of this filter is not recommended.)

The contribution of nitrogen dioxide to the oxidant reading is determined by measuring the instrument response to a known stream of NO_2 and concurrently analyzing for NO_2 in the atmosphere. The appropriate subtraction can then be made to correct for NO_2 interference.

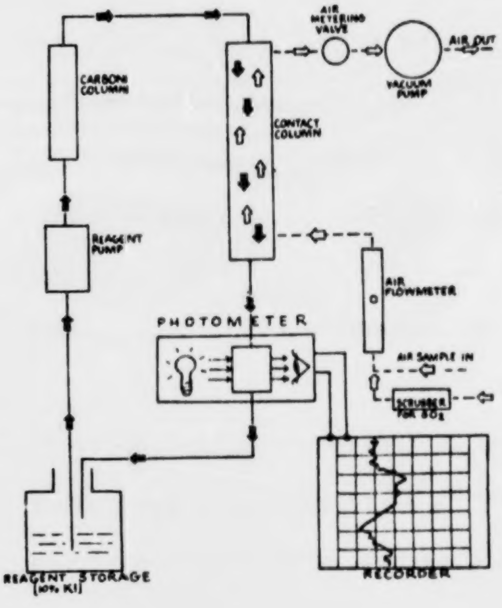

AIR METERING VALVE
AIR OUT
CARBON COLUMN
VACUUM PUMP
CONTACT COLUMN
REAGENT PUMP
AIR FLOWMETER
PHOTOMETER
AIR SAMPLE IN
SCRUBBER FOR SO2
REAGENT STORAGE [10% KI]
RECORDER

Figure 3.9. Schematic of colorimetric oxidant analyzer

Disadvantages of colorimetric oxidant analyzers are need for rigid maintenance including changing of reagent, carbon column, pH adjustment, lubrication of moving parts (pumps) and leak checks. Other disadvantages are sensitivity of flow systems, non-specificity and fragility of components.

3.6.1.3.2 Amperometric Analyzers--Amperometric analyzers measure the current necessary to maintain halogen concentration at a fixed level, the current being proportional to the amount of absorbed reactant. Analyzers operating on this principle are often referred to as "coulometric" analyzers. In coulometry, the quantity of electons necessary to oxidize or reduce a substance is measured. Because it is the current and not the charge which is measured, "coulometric" analyzers are more properly called amperometric analyzers.

Oxidant amperometric analyzers operate on the principal that O_3 and other atmospheric oxidants in an air sample react with iodide ions in the sensing reagent to produce iodine which forms the tri-iodide ion (I_3^-). The tri-iodide ion in turn is electrically converted back into iodide ions through cathodic reduction using either an electrolytic (Brewer or Schulze) cell or a galvanic (Hersch) cell.

3.6.1.3.3 Electrolytic Analyzers--For about fifteen years Mast Development Company has sold an O_3 analyzer with Brewer-type cell. It is portable, can be operated off batteries or line voltage and costs about $1,000. Hundreds have been sold.

In the Mast O_3 analyzer an iodine-containing electrolyte is used. A potential (approximately 0.25 V) is applied between electrodes. The initial current polarizes the cathode with a layer of hydrogen (H_2)

which prevents further current flow. Tri-iodide ion produced by the reaction between oxidant or ozone and KI immediately reacts with the H_2 to depolarize the cathode. Consumption of hydrogen causes flow of polarization current to replace the reacted hydrogen and reestablish polarization.

The polarization current is proportional to the tri-iodide ion concentration according to the configuration of the electrodes. The reaction at the electrodes gives an electron yield less than 100% of theoretical and must therefore be calibrated with a known ozone source. This technique is now used in the Intertech, Mast and Welsbach amperometric analyzers.

3.6.1.3.4 Chemiluminescent Analyzers--In the early 1960's a detector based on measurement of chemiluminescent emissions from the reaction between O_3 and Rhodamine-B was constructed by Regener. The concept of chemiluminescence for O_3 detection went through a number of stages as variants were explored. Nederbragt did initial work on a gas-phase analyzer which is the choice approach based on number of analyzers in use (over five hundred) and manufacturer numbering about 10. It is also the reference method designated in Federal Register, 36 (89), April 30, 1971.

The reaction between ozone and ethylene yields chemiluminescent emission in the 300 to 600 nm region with maximum intensity at 435 nm, intensity being proportional to the ozone concentration. Figure 3.10 is a diagram of a typical gas-phase (ozone-ethylene) chemiluminescent ozone analyzer. The detector resonds linearly to ozone concentrations from 0.002 to above 5 ppm; there are no apparent interferences. Small improvements in sensitivity result from cooling the phototubes used to detect emitted light or by increasing the ethylene flow rate.

Using pressurized cylinders of ethylene is prohibited in many locations by OSHA regulations and local fire codes. Using the cylinder may require construction of an external housing that is well-ventilated, adequately secured and protected from flame or excessive heat, with flow-limiting orifices at the cylinder outlet. Leak-free corrections are essential. An alternative is a blend of ethylene and inert gas that is flammable but not explosive. Requirements for storage and use of this gas are less stringent, and satisfactory analyzers are available.

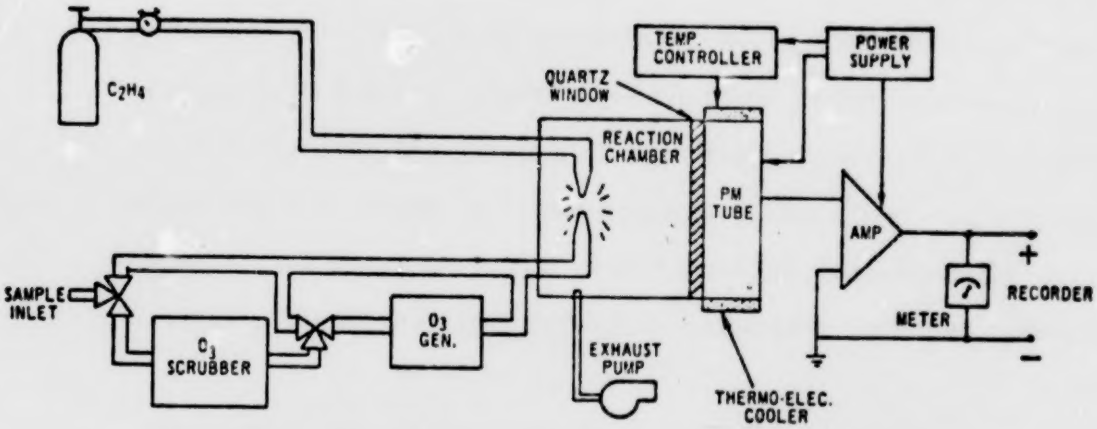

C_2H_4
QUARTZ WINDOW
TEMP. CONTROLLER
POWER SUPPLY
REACTION CHAMBER
PM TUBE
AMP
+
SAMPLE INLET
RECORDER
METER
O_3 GEN.
O_3 SCRUBBER
EXHAUST PUMP
THERMO-ELEC. COOLER
−

Figure 3.10. Automated gas phase chemiluminescent ozone monitor

Chemiluminescent methods for monitoring ozone other than the O_3:C_2H_4 reaction are now available commercially. Philip Eindhoven of the Netherlands has developed an ozone monitor based on the classical Rhodamine-B ozone reaction. His system is automatically calibrated one an hour due to the change in response characteristic of the Rhodamine disc used. This monitor is being sold in Europe but not yet in the U.S.

3.6.1.3.5 Ultraviolet Absorption Ozone Analyzer--Dasibi, Inc. sells an O_3 analyzer that continuously monitors O_3 in the air with parts per million readable directly from the front panel. An analog output is available for continuous strip-chart recording, as well as a binary-coded-decimal (BCD) output for direct interfacing with a computer or a printer. It is sensitive to 0.01 ppm O_3 and reads to 9.99 ppm. A schematic of the instrument is shown in Figure 3.11. This unit employs modern electronic circuitry, including a stabilized mercury UV light source, dual detectors, digital electronics, and signal integration. The sampled air is pumped into the instrument at a flow rate of approximately 1 liter/minute. The sample stream alternately bypasses and then passes through the catalytic converter, which removes O_3 selectively. This air sample, stripped of O_3, enters the absorption cell in which the photodetector measures the amount of UV light transmitted through the cell, measured at 253.7 nm. The result is stored as the reference measurement and includes effects due to other pollutants present in the sample stream. The next cycle brings the air sample directly into the absorption cell. The detector now measures attenuated ultraviolet light due to O_3 in the sample stream and a subtraction is made from the stored reference measurement. The difference is ozone concentration.

The ultraviolet absorption technique has the advantage over chemiluminescence that it requires no reagent; it has the disadvantage that very high concentrations of certain hydrocarbons or mercury vapor may be interferences.

3.6.2 Stationary Sources

Since publication of the "Air Quality Criteria for Particulate Matter" in January, 1969, EPA has published (December 23, 1971, Federal Register) methods for finding the rate of particulate emission from certain stationary sources.[10] Methods one through four are for obtaining the number and location of sampling points, stack velocity, stack gas molecular weight and stack gas moisture. Method five is for obtaining the mass concentration of particulate emissions. Using these five methods, the emission rate of the source being tested can be determined.

These methods were prescribed for compliance testing of sources covered under the Standards of Performance for New Stationary Sources as described in the Clean Air Act. The first sources covered were steam generators, Portland Cement plants and incinerators. Standards for particulate emissions from a second group of six industries were promulgated in the FR March 8, 1974.[11]

In addition to use in measuring particulate emissions from new sources, Method five has been widely used on existing sources and is the method used by many state and local agencies. When the sampling conditions are met as described in the Federal Register, it is applicable to most types of stationary sources, although special problems will require adaptation or use of an alternate procedure.

Evidence shows excellent analyzer repeatability. Some EPA scientists suggest that an accurately calibrated analyzer can be taken into the field with an ozone generator and used as a secondary standard to obtain a multipoint (typically seven) calibration curves for field analyzers. Returned to the laboratory, the Dasibi analyzer calibration could be reestablished. It is contended this would be an excellent way to maintain the accuracy of field O_3 analyzers.

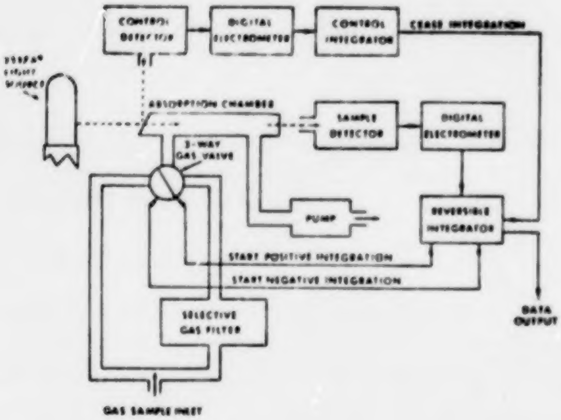

CONTROL DETECTOR
DIGITAL ELECTROMETER
CONTROL INTEGRATOR
CEASE INTEGRATION
ABSORPTION CHAMBER
SAMPLE DETECTOR
DIGITAL ELECTROMETER
3-WAY GAS VALVE
PUMP
REVERSIBLE INTEGRATOR
START POSITIVE INTEGRATION
START NEGATIVE INTEGRATION
SELECTIVE GAS FILTER
DATA OUTPUT
GAS SAMPLE INLET

Figure 3.11. Ultraviolet absorption ozone analyzer

EPA is working on UV spectrophotometric methods for absolute determination of ozone generator output and preliminary results suggest it may be possible to make such determinations in the 50 ppb ± 10% range with relatively inexpensive instruments.

Several other methods are being or have been studied as alternate methods for stationary source particulate emission measurement. In-stack filter methods are promising. The current ASTM method uses an in-stack Alundum thimble to collect the particulate matter.[12] As with most methods, in-stack methods are not suited for all sources.

Several instrumental methods are available also, with instruments based on beta radiation attenuation (beta gauges) now being produced commercially. While the beta gauge can yield accurate measurements, its use, like other extractive methods, depends on obtaining a representative sample in the measuring zone. This is a difficult problem.

To overcome errors inherent in the use of current sampling equipment, improved in-stack devices and non-extractive optical devices are being developed. Reviewing the state of the art of instrumental methods for particulate emissions for combustion sources has been done on an EPA contract.[13]

Besides determining total mass, measure of particle size distribution is of major importance for future regulations on fine particle emission. Most size measurements are now made by inertial sizing devices. An EPA study of most of the commercially available devices was made by contract.[14] Other approaches to size distribution measurement including optical methods are being studied. Volume III of reference four describes many of these methods, as does the NERC/RTP briefing report on fine suspended particulate matter.[15]

Method eight published in the December 23, 1971, FR measures SO_3 and H_2SO_4 from a sulfuric acid plant. Except for this method and methods published for hazardous air pollutants mercury and beryllium, no methods to determine composition of particulates emitted from stationary sources have been prescribed. For data on chemical composition, particulate matter collected by either Method five or other methods is generally analyzed by standard methods, as for sulfates and nitrates. No new approaches for these two not included in the NERC/RTP task force report are available.[16,17]

Presently, x-ray fluorescence (XRF) spectroscopy is the most attractive method for routine multielemental analysis of particulate matter, as shown in a study carried out by EPA interagency agreement with the Naval Research Laboratory. A first phase report[18] described the laboratory evaluation of XRF for elemental analysis of filter-deposited particulate material. A later report[19] demonstrated the usefulness of simultaneous multispectrometer instruments available from x-ray equipment manufacturers, for large-scale routine analysis. More recently a small, low-powered portable XRF analyzer was designed and a prototype instrument built to show applicability of the x-ray technique to on-site use.

3.7 SUSPENDED PARTICULATE

Current research is advancing our understanding of the sources, properties, chemical composition and dynamics of the atmospheric aerosol or total suspended particulate matter. Progress has been made in establishing multimodal distribution of the atmospheric aerosol, the typical observation of a biomodal mass-size distribution and differences in chemical composition, identification of organic material as a major primary and secondary component of fine particulate matter, and development of improved instruments and techniques for measuring aerosol parameters.

3.7.1 Calibration

For suspended particulate, the concept of calibration needs special attention. Methods in air pollution are generally designed to be specific for an element, compounds or class of compounds. All substances in the air above a certain diameter may be considered, for some purposes, as suspended particulate. There are many devices for collecting airborne particulate. The mass, density, surface area, electrical charge and shape of a particulate are properties that may determine sample design characteristics and collection efficiency. Operating principles of remote sensing devices may depend on color, refractive index, opacity, light scattering, or even attenuation of ultrasonic frequencies. Calibration techniques may vary with the type of instrumentation, but will usually involve the generation of aerosols or particulates of known physical and chemical properties. For example, polystyrene latex spheres of known diameters are available and useful for calibration of particle size analyzers.

3.7.2 Ambient Air

3.7.2.1 Impactor Measurements of Size Distribution--EPA has completed tests on impactors showing that apparent size distribution can be seriously affected by the type collection surface used. A Cascade impactor with silicone grease-coated-aluminum collection surface was compared with an identical Cascade impactor with either glass fiber or clean aluminum collection surfaces. For the greased collection surface, it was seen that apparent mass median diameter is decreased by factors two to three, when clean aluminum and glass fiber collections are used respectively. Serious particle-bounce errors can occur in conventional impactors when a greased collection surface is not used.

3.7.2.2 Virtual Impactor Optimization--To eliminate particle bounce errors associated with conventional impactors, in a virtual impactor size fractionation is accomplished aerodynamically without the aid of an impaction surface. In this device, particles are collected by filtration downstream of the fractionator. The Lawrence Berkeley Laboratory has studied loss mechanisms for the virtual impactor and and developed methods to lower losses for particles smaller than 20 μm.

3.7.2.3 Automated Dichotomous Samplers--Twelve automated samplers to separately collect particles in the 0-2 and 2-20 μm size range have been fabricated and will be operated in St. Louis beginning November 15, 1974. The devices use a virtual impactor for size fractionation. Automated sample changing allows collection of up to 35 aerosol samples for sampling intervals adjustable from two to 48 hours.

3.7.2.4 Manual Dichotomous Samplers--A sampler for collecting particles for 24-hour intervals in the 0-3.5 and 3.5-20 μm range is being developed for health effect measurements and routine monitoring. A virtual impactor is used for size fractionation. A prototype is being tested. An improved device with flow rate regulators is under development and will be tested in 1975.

3.7.2.5 Beta Gauges--A number of beta gauge devices for measuring particulate mass collected on a filter are presently being tested. These devices consist primarily of a radioactive ^{14}C source and a solid state detector. Although the beta gauge method is not necessarily more accurate than a gravimetric method, it is much better adapted for low-cost automated and semicontinuous measurements. Documentation of field accuracy will become available in 1975.

3.7.2.6 X-Ray Fluorescence Analysis--X-ray fluorescence spectrometers are used routinely to determine concentrations of elements with atomic numbers above 19. Procedures for obtaining quantitative analysis for elements with atomic numbers between 13 and 19 are being developed. Good sensitivity for sulfur is obtained using both energy dispersive and wavelength dispersive techniques. More than ten laboratories were actively using this technique during 1974.

3.7.2.7 Measurement of Visibility Reduction due to Aerosols--Recent studies show good agreement between human observer and time averaged integrating nephelometer measurements of visibility. However, gravimetric measurement of total suspended and fine particulates we find to be only a fair measure of visibility.

3.8 SULFUR OXIDES

3.8.1 Ambient Air

3.8.1.1 Sulfur Dioxide--A new technique to measure SO_2 has been developed by the National Bureau of Standards based on measuring the fluorescence of SO_2 induced by exposing SO_2 to ultraviolet monochromatic radiation. The fluorescence emission is a linear function of SO_2 concentration. Systems to measure both ambient and source concentrations of SO_2 using this principle are now commercially available. This system is virtually flow insensitive, a major advantage over other SO_2 monitoring principles.

Under EPA sponsorship an ultra-sensitive flame photometric detector has been developed to measure 0.1 ppb of SO_2. The system uses a pair of rare earth optical filters which measures the ratio of emission of the SO_2 luminescence to background flame signal. This ratio measurement improves sensitivity and specificity of the flame photometric detector for SO_2. The detector has applications in areas where background concentrations of SO_2 are needed.

3.8.1.2 Sulfates--Various classical colorimetric and turbidimetric methods of measuring sulfates are being compared to measurements of total sulfur by x-ray fluorescence (XRF). Each study is intended to establish the limitations of classical methods for sulfates and to yield data on the applicability of XRF methods for sulfate analysis of particles collected from the atmosphere.

3.8.1.3 Sulfuric Acid--An automated instrument has recently been developed which collects sulfuric acid from ambient air on an inert teflon surface. Sulfuric acid is separated from other particulates by volatilizing it with warm, dry air. The sulfuric acid volatilized is determined with a flame photometric detector sensitive to sulfur-containing compounds. The system is capable of measuring 0.1 ugm/m^3 of H_2SO_4. EPA is working to characterize and improve the instrument's performance for use as a routine field monitor.

3.8.2 Stationary Sources

The SO_2 compliance test method (Method six, Federal Register, December 23, 1971) involves gas sample extraction from a source and measurement by the barium thorin titration procedure.

In addition to compliance testing for SO_2 the December 23, 1971, FR requires continuous monitoring for the pollutant gas. Proposed emission monitoring and performance testing requirements for SO_2 (NO_x, CO and H_2S) continuous monitoring systems were published in the September 11, 1974, Federal Register. The approach taken by EPA requires each source owner or operator to demonstrate the capability of continuous monitoring systems to meet the proposed performance specifications for his particular source.

Research since 1972 into new analytical techniques for SO_2 source measurement has been active. The UV fluorescence technique for source and ambient SO_2 levels has been demonstrated and is now available in a commercial instrument system.

The feasibility of using a PbSnTe-diode laser system for SO_2 source measurements has also been shown. A present liability of the technique for field use is the necessity for liquid helium temperature operation.

Under an EPA contract Burch and Gryvnak[8] have applied gas filter correlation techniques for in-stack measurement of SO_2, NO, HF and HCl. Field evaluation is being done by EPA personnel.

The Barringer correlation spectrometer system for the remote detection of SO_2 was evaluated and appears to have serious drawbacks and seems unusable for enforcement or research.

The general technique of gas filter correlation appears quite promising for the remote sensing of gaseous pollutants. An EPA contract has developed a remote sensor for SO_2. The sensor is relatively small (25 lbs., 1 cu. ft.), simple to operate and field usable with battery operation. It has undergone field testing at a California oil-fired power plant and a North Carolina coal-fired power plant. Comparative SO_2 measurements for Method six, a continuous in-stack monitor and the gfc remote sensor gave relatively good (±15%) agreement among the three techniques.

3.8.3 Mobile Sources

Sulfur in fuel is normally determined by one of several methods including x-ray (ASTM P-2622), lamp (ASTM P-1266), and bomb (ASTM P-129). Micro coulimetric and x-ray fluorescence methods have also been employed. The latter technique yields quick qualitative and quantitative information, but is difficult to use with leaded fuels because of peak overlaps of lead and sulfur. High resolution x-ray fluorescence instrument appears to have overcome this difficulty.

As yet, there is no standard procedure for sampling and analyzing sulfur oxide emissions from mobile sources. Most earlier data on sulfur oxide emissions were obtained using modifications of the Federal testing procedure for sulfuric acid mist and sulfur dioxide emissions from stationary sources. In most cases raw exhaust is sampled by inserting a sample probe anywhere between the exhaust manifold and the tail pipe. The exhaust sample is drawn from the probe through a heated sample line at a constant flow rate into a series of impingers containing 80% isopropanol solution and 3% solution of hydrogen peroxide to selectively collect SO_3 and SO_2 respectively. The SO_2 is oxidized to sulfate and is retained as such in the hydrogen peroxide solution. The sulfate content of the impingers is determined for SO_3 and SO_2 by barium perchlorate or barium chloride titration using thorin as indiator; variation involves insertion before the impingers of a controlled condensation coil with a fritted filter at the end. By controlling the condenser temperature between 60 to 90°C, sulfuric acid can be removed by condensation and filtration.

Another sampling technique which has gained popularity lately is the dilution tunnel method. Raw exhaust from the tail pipe is fed into a dilution tunnel where it is mixed with a stream of clean air and drawn through the tunnel by a pump at the opposite end. A nominal ten-to-one dilution is normally attained. The temperature of the exhaust drops during expansion and dilution with clean air in the tunnel, resulting in formation of sulfuric acid mist. Sample probes protrude into the air stream at the far end of the tunnel and sample the air-exhaust mixture in the tube proportionally and isokinetically. Particulates, including H_2SO_4 aerosols, are trapped on the filter in the sample probe. SO_2 is collected by absorption in dilute aqueous sodium tetrachloromercurate and determined by the standard West-Gaeke pararosanilive method.

In recent months, instrumentation for in-line monitoring of SO_2 has become commercially available. The principle is based on fluorescence of SO_2 when pulsed irradiated with light of a certain wavelength. Original application is in-stack monitoring of SO_2 where the concentration is in the hundreds ppm range, but adaptation to SO_2-monitoring in mobile exhaust is a promising possibility.

The analysis of SO_2 by oxidation to sulfate and titration with barium ion in the presence of a suitable color indicator or by the West-Gaeke pararosanilive technique is straightforward. Sampling and collection techniques appear to be a major source of problems in the overall analytical scheme. Concentration of SO_2 in auto exhaust is high enough that titratable quantities can be collected within a reasonable time frame.

Analysis of SO_3 on soluble sulfates in automobile exhaust presents a much harder problem, especially for cars not equipped with catalyst. The amount of soluble sulfate varies from almost nothing to a maximum of about 2% of the total sulfur burned. In a simulated urban driving cycle, the amount of sulfate particulate sample collected on a 47 mm filter by sampling tunnel diluted exhaust at flow rate of 1 cfm may total no more than 10 micrograms as SO_4. This amount is much lower than the sulfate background of some filter collection media, especially glass fiber filter. Compounding the problem is the fact that this amount is usually beyond the detection limit of most existing analytical methods of sulfate.

The choice of filter media for particulate sulfate is quite critical at low concentrations. At high concentrations, the media background may be reduced to negligible levels by proper dilution. Even supposedly low sulfate background glass fiber filters were found to contain greater than 30 micrograms per 47 mm diameter filter.

Fluoropore, a Teflon filter with polyethylene backing, had almost zero sulfate background. It is available in large enough nominal pore size to permit sampling at a reasonable flow rate without excessive pressure drop and is inert to most solvents. One disadvantage, however, is that only solvents with low surface tension, such as isopropanol or methyl alcohol, or mixtures of these with water, can be used to extract the samples from the filter. The filter also curls up after removal from the holder, thus presenting problems for mounting the filters on cassettes to do x-ray fluorescence analysis.

Nucleopore, a polycarbonate filter, is another good candidate for filter medium. It has low sulfate background and remains relatively smooth after removal from the filter holder. The only drawback for mobile source sampling is an excessively high pressure drop during sampling.

Most analytical methods for soluble sulfates involve so much sample handling--extraction, rinsing, evaporation and concentration, pH adjustment--that the possibility of sample losses during a handling process is increased. X-ray fluorescence would obviate most of the handling steps, but has a rather stringent requirement for filter samples. In most cases only a certain area of the filter is examined and the deposits are assumed to be uniform. Filters must be reasonably flat and free from wrinkles. Preliminary analysis of K_2SO_4 aerosols generated in a bag and collected both on fluoropore and Nucleopore filters show better correlation between x-ray and gravimetric measurements with Nucleopore filters than with Fluoroposre filters. At high sulfate loadings, x-ray fluorescence gave lower values than gravimetric measurements.

The collection of SO_3 in exhaust via absorption in 80% isopropanol is reported to result in high sulfate values. Apparently, some SO_2 is retained, partly oxidized to SO_4, or the resulting sulfite responds quantitatively to barium ion tritration. This problem becomes acute when baseline data are being generated with low sulfur fuel and non-catalyst cars.

The Mobile Source Measurements Research Section has developed an automated version of the barium chloranilate method for sulfates applicable to soluble particulate sulfate from cars run on non-leaded fuels. It is based on the reaction of sulfate ions with the solid barium salt of chloranilic acid. The reaction precipitates out $BaSO_4$ and releases highly UV nm and related to sulfate concentration. The sensitivity of the method is greatly enhanced by conducting the reaction in a medium less polar than water, such as ethanol-water or isopropanol-water mixtures, where the solubilities of both $BaSO_4$ and barium chloranilate are reduced. Sensitivity of the method is better than 0.5 μg SO_4/ml of the extracting solution.

Exhaust samples diluted in a tunnel are collected on Fluoropore filters, extracted with 60/40 isopropanol/water mixture and injected into a liquid chromatographic system. The sulfate sample is fed through a strong cation exchange resin in hydrogen form to remove cationic interference and then through a column of barium chloranilate where color reaction takes place. $BaSO_4$ is retained in the column and the colored species is measured with a UV-monitor at 310 nm. Through-put time from initial sample injection is less than four minutes and sensitivity is better than 0.5 μg SO_4 per ml of extracting solution. Precision obtained in early work was about ±.05 μg $SO_4^=$/ml. There are ionic interferences from such anions as cl^-, Br^-, F^- and $PO_4^{\equiv}$. For exhause samples from cars run on non-leaded fuels, ionic interference is minimal.

3.9 ASBESTOS

3.9.1 Stationary Sources

The present NESHAP regulation for asbestos, based on prescribed control practices rather than maximum permissible emission levels, is partly the result of inadequate methods for measuring airborne asbestos concentrations. It is generally agreed that more satifactory asbestos measurement methods than now exist are need both for (a) rapid routine screening purposes (to detect sources, measure ambient levels or implement an emissions standard), and for (b) research applications (e.g. in support of health effects studies) where maximal information on fiber count and size distribution are required. A new x-ray diffraction technique is being developed as a rapid screening procedure though an interagency agreement with the Naval Research Laboratory. For research applications, however, and possibly also as a reference procedure, it is likely that one or more of the current electron microscope (EM) techniques will be used for an indefinite future period.

Problems associated with EM methods are well known. The procedures are tedious, expensive (about $250 per sample) and time-consuming (about one man-day or more per sample). Each of the steps in an EM assay, e.g. sample acquisition and treatment, specimen preparation, morphological and confirmatory identification, fiber counting and sizing, etc., can be the source of error. A chaotic situation exists because there are probably a dozen EM procedures in use that differ with respect to one or more of the steps cited above and there has been no attempt to establish the accuracy or precision of the various methods. There is an urgent need to establish a single EM procedure as acceptable standard analytical technique so that valid comparisons can be made of data obtained by different laboratories.

The feasibility of a new x-ray diffraction (XRD) technique as a rapid screening method has been shown. The approach consists of measurements in a specially-designed broad-beam diffractometer after samples have been pretreated to align asbestos fibers. Measurements with standard chrysotile samples indicate a detection limit of about 0.3 μg for a 500-second measurement time. During FY 1975 a prototype XRD asbestos analyzer based on this principle will be built for delivery to ERC/RTP and testing with field samples by the Chemistry and Physics Laboratory.

3.10 BERYLLIUM

Methods 103 and 104 for measuring beryllium emissions from stationary sources are described in the Federal Register.[20] These methods are applicable to all tests for beryllium required under Part 61, National Emission Standards for Hazardous Air Pollutants. Presently, Part 61, Subparts C and D, requires control of beryllium emissions from the following beryllium-handling activities: extract and ceramic plants, foundries, incinerators, propellant plants, machine shops and rocket motor test sites. A background information document[21] issued with the regulations describes the development of standards. Test methods require a representative portion of stack gases to be removed from the stack and filtered, with filtered material analyzed for beryllium content.

Developing instrumentation to continuously monitor particulate matter, including beryllium, was conducted under contract. The principal objectives applied to beryllium emissions were two: (1) to prepare a document on the status of the problem of continuous monitoring and (2) to produce a prototype monitoring system.

The study identified various methods available, but concluded that no one method is applicable to the concentrations and types of beryllium particulates existing in stack gases today. The work of Webb, et al.[22], suggests a continuous monitor based on emission spectroscopic measurements of a continuous flowing (40 l/min.) sample stream of stack gases. Such an emission spectroscopic measurement can provide a means of monitoring beryllium or most other metallic elements and some non-metals simultaneously. The technique has the necessary (a) selectivity, (b) speed (30 sec.) for rapid repeated analyses, and (c) sensitivity (1 $\mu g/m^3$). A method based on the $^{9}Be(\alpha,n,\gamma)$ ^{12}C reaction can be used for measuring beryllium continuously in atmospheres or stack gas emissions containing principally beryllium or its compounds down to 1 $\mu g/m^3$, but cannot be used where other particulate matter is present in large amounts. A prototype proved not feasible at this time due interfering particulate matter.

3.11 MERCURY

The National Emission Standard for mercury promulgated in April, 1973, is applicable to stationary sources processing mercury ore and those using mercury chlor-alkali cells to produce chlorine and alkali metal hydroxide. Reasons for selecting these soures for regulation and excluding other mercury sources are stated in the background document issued with the first group of NESHAPS standards.[21] The standards, stack sampling procedures and reference measurement methods are prescribed in the Federal Register.[20] The reference methods are manual procedures based on isokinetic collection of particulate and gaseous emissions in acidic iodine monochloride solutions. Method 101 is for sampling air streams and Method 102, for hydrogen streams encountered in chlor-alkali plants.

Caution must be exercised in applying this method to other than regulated sources. For example, if the sampling stream contains high sulfur dioxide concentrations, such as are present in fossil fuel power plants and non-ferrous smelters, the efficiency of collection is questionable due to reaction of the SO_2 with ICl Impinger solution. Sulfur dioxide scrubbers such as sodium carbonate solutions have been placed in the front of the sampling train and are reported to overcome this problem.[23,24]

Optical instrumentation has been the most universal approach in mercury analysis and monitoring. Optical techniques utilize the strong ultraviolet absorbance of mercury vapor at 253.7 nm. Since mercury is an atomic species, it absorbs and emits energy at the same frequency. The extinction coefficient for mercury is approximately $4x10^6$.0. While the technique is not specific for mercury, its strong absorpiton allows mercury to be determined in the presence of 100-1000 times the concentration of weakly-absorbing species. (This is not enough for non-ferrous smelters and power plants which emit mercury in low concentrations in the presence of high levels of sulfur dioxide.)

UV analyzers are available commercially in single beam, dual wavelength and dual beam configurations. To increase the rejection ratio for interferences and make the instruments more specific for mercury, one approach uses Zeeman splitting of the mercury resonance line while another makes uses pressure broadening of the 253.7 nm mercury line. A third approach to improve specificity involves isolation of mercury by absorption on a noble metal (silver or gold) collector and subsequent therman desorption and analysis.

The laboratory phase of the EPA-funded study included development of a mercury generation system, measurement of interferences and evaluation of pyrolyzers to decompose hydrocarbons and convert mercuric compounds to elemental mercury and evaluation of scrubbers to remove sulfur dioxide. These data were obtained for each instrument: accuracy, precision, sensitivity, stability, interferences, reliability and sample treatment required. The laboratory test program was followed by field tests at three mercury sources: (1) secondary processing of mercury; (2) chlor-alkali production; and (3) non-ferrous (zinc) smelting.

Precision and accuracy of monitoring instruments is greatly affected by the sampling interface system and its ability to transport a representative sample. Mercury concentrations sampled in the field ranged as high as 40 mg per cubic meter, requiring a dilution system capable of controlling mercury concentration in the range of the instruments (normally)-1.0 mg per cubic meter). The system used in the field performed less than adequately to satisfy these requirements, but sample treatment for interfering species and conversion of particulate and organomercury compounds to elemental mercury was accomplished successfully. Laboratory results indicated that a sodium carbonate scrubber absorbed sulfur dioxide without removing mercury,

All species of mercury tested were converted to elemental mercury by pyrolysis in a catalytic converter. Hydrogen stream test results showed that mercury species other than elemental mercury were present so that total mercury monitoring of chlor-alkali hydrogen lines would require some means of gas stream pyrolysis to convert particulate mercury or organomercury species to elemental form.

It was found that available mercury-measuring instrumentation can be adapted to measure total mercury emissions from certain stationary sources, particularly chlor-alkali plants. The transporting and conditioning of the sample poses difficulties requiring more research. The need for a dynamic dilution system to condition high-level mercury emissions sets the requirement for a fairly sophisticated automatic interfacing subsystem.

3.12 METHODS STANDARDIZATION AND PERFORMANCE EVALUATION

3.12.1 General Discussion

EPA is working to standardize reference methods for industrial air pollutants in ambient air and stationary and mobile sources. The program involves in-house methods evaluation and ruggedness testing, method inter-relativity studies and collaborative testing. All criteria pollutants are under study, and some results have been published for all six criteria pollutants.

3.12.2 Particulates

After reference method was tested by 12 laboratories, statistical analysis of the resulting data showed:[25]

1) Relative standard deviation for single analyst variation is 3.0%.

2) Relative standard deviation for multilaboratory variation is 3.7%.

3) Minimum detectable amount of particulate matter is 3 mg, equivalent to 1-2 $\mu g/m^3$ for a 24-hour sample.

3.12.3 Sulfur Dioxide

The 30-minute sampling option prescribed in the reference method was collaboratively tested by 14 laboratories and a statistical analysis of that data showed:[26]

1) Standard deviation for within-laboratory variation varies linearly with concentration from 15 $\mu g/m^3$ at zero to 36 $\mu g/m^3$ at 1000 $\mu g/m^3$.

2) Standard deviation for between-laboratory variation varies linearly with concentration from 29 $\mu g/m^3$ at zero to 70 $\mu g/m^3$ at 1000 $\mu g/m^3$.

3) No systematic error, bias or inaccuracy was detected and the lower limit of detection is 25 μg/m^3 (95% confidence level).

The 24-hour sampling option prescribed in the reference method was collaboratively tested by four laboratories and a statistical analysis of the data shows:

1) Standard deviation for within-laboratory variation varies linearly with concentration from 18 μg/m^3 at 100 μg/m^3 to 51 μg/m^3 at 400 μg/m^3.

2) Standard deviation for between-laboratory variation varies linearly with concentration from 37 μg/m^3 at 100 μg/m^3 to 104 μg/m^3 at 400 μg/m^3.

3) The 24-hour sampling method apparently has a concentration-dependent bias which becomes significant at the 95% confidence level at about 400 μg/m^3. Observed values tend to be lower than expected SO_2 concentration levels.

4) Comparison of results from 30-minute and 24-hour sampling options shows the 24-hour procedure to be more precise than the 30-minute procedure. However, these differences are based on tests of differing experimental design. Although accepted statistical techniques were used to process the data, the exact degree of improved precision is uncertain.

3.12.4 Carbon Monoxide

The reference method was collaboratively tested by 16 laboratories and statistical analysis of the data showed:[28]

1) Standard deviation for within-laboratory variation is 0.57 mg/m^3 (1 ppm CO equals 1.15 mg/m^3 CO).

2) Standard deviation for between laboratory variation varies nonlinearly with concentration with a minimum of 0.85 mg/m^3 at 20 mg/m^3 and ranges as high as 1.54 mg/m^3 in the concentration range of zero to 60 mg/m^3.

3) The minimum detectable limit is 0.3 mg/m^3.

3.12.5 Nitrogen Dioxide

Evaluation shows the sodium arsenite manual procedure for measurement of ambient NO_2 has a high, constant collection efficiency of 82% over its range of 20 to 750 $\mu g/m^3$ NO_2.[29] The method is insensitive to normal variations in orifice bubbler diameter, temperature of absorber solution during sampling and concentration of sodium arsenite. No and CO_2 were confirmed as positive and negative interferents, respectively.

Evaluation shows the TGS-ANSA manual procedure for ambient NO_2 has a high, constant collection efficiency of 93% over its range of 20 to 700 $\mu g/m^3$ NO_2.[30] The method is insensitive to normal variations in time between sample collection and analysis, storage conditions after sample collection, flow rate, CO_2 concentration, sampling time and orifice size. The time interval between addition of the diazonium salt forming reagent and the diazonium salt coupling reagent is critical and must be carefully controlled.

Evaluation shows the Triethanolamine (TEA) manual procedure for ambient NO_2 has a constant collection efficiency over its range of 20 to 700 $\mu g/m^3$, both with and without added n-butanol using either frits or restricted-orifice bubblers.[31] The collection efficiency using frits is about 80%, while the efficiency drops to about 50% using restricted-bubblers. More work is not contemplated because other methods show more promise for measurement of ambient NO_2.

3.12.6 Stationary Sources

EPA test methods promulgated for use in the determination of emission levels specified in the New Source Performance Standards were collaboratively tested by four teams simultaneously sampling emissions from a fossil fuel-fired steam generator.[32] Tested were Method seven (Oxides of Nitrogen), Method six (Sulfur Dioxide) and Method five (Particulates). Conclusions derived from the data are:

1) Method seven (NO_x). Estimated within-laboratory standard deviation is 6.6% of the mean of values measured and estimated between-laboratory standard deviation is 9.5% of the mean of values measured. Estimated minimum detectable limit is 5.33×10^{-7} lb/scf.

2) Method six (SO_2). The method is accurate below 300×10^{-7} lb/scf, but shows significant negative bias in the range $300\text{-}500 \times 10^{-7}$ lb/scf. Estimated within-laboratory standard deviation is 4.0% of the mean of the values measured and estimated between-laboratory standard deviation is 5.8% of the mean of values measured. Estimated minimum detectable limit is 3.16×10^{-7} lb/scf.

3) Method five (Particulates). Estimated within-laboratory standard deviation is 31.1% of the mean of values measured and estimated between-laboratory standard deviation is 36.7% of the mean of values measured.

EPA test Method five (Particulates) was collaboratively tested at a municipal incinerator by having four teams simultaneously sample particulate emissions.[33] Estimated within-laboratory standard deviation is 25.3% of the mean of the values measured and estimated between-laboratory standard deviation is 38.7% of the mean of measured values.

In tests at a nitric acid plant[34] estimated within-laboratory standard deviation is 14.9% of the mean of measured values and estimated between-laboratory standard deviation is 18.5% of the mean of measured values.

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4. ENVIRONMENTAL APPRAISAL

4.1 SOURCES

4.1.1 National Emissions Report

National Emissions Reports estimate source emissions of those air pollutants for which national standards have been promulgated. The criteria pollutants are particulates, sulfur oxides (SO_x), nitrogen oxides (NO_x), hydrocarbons (HC) and carbon monoxide (CO). The reports are compiled from source information of the National Emissions Data System (NEDS). Compilations are presented for the nation, for individual states, for Air Quality Control Regions (AQCRs) and for interstate AQCR portions. This first annual report represents the best available indicators of national emissions for the calendar year 1972. The estimates reported are based on source records in NEDS prior to receipt of the December 31, 1973, Semiannual Report. Thus, the data are generally comparable to data collected for the development of State Implementation Plans (SIPs), but include revisions and updates whenever available.

The NEDS point source file contains data on stationary facilities that are individual emitters of relatively large quantities of one or more air contaminants. A point source is often arbitrarily considered to be a facility in which the total annual emission of any one criteria pollutant equals or exceeds 100 tons per year. In general, individual

emission points are defined as those annually emitting one or more pollutants equal to or greater than 25 tons per year. In certain instances, possible significant contributors, although emitters of lesser annual amounts, are accorded point source designation.

At the present time, NEDS contains data for approximately 75,000 emitting points in all states, the District of Columbia and three territories. Considerable information is stored for each point source; for example, data on annual operating rates or activity levels (i.e., amount of fuel consumed by a boiler, or quantity of product produced by an industrial process, etc.). Information on existing air pollution control devices and their efficiencies is also recorded. These and similar data are subsequently used in determinations of source emission according to procedures outlined in the following discussion of the NEDS emission factor file.

Area sources are all other emissions sources not identified as point sources. For example, the NEDS area source file contains data on all mobile sources (motor vehicles, aircraft, railroads, etc.), small stationary sources, and miscellaneous sources such as forest fires, agricultural burning and retail gasoline marketing operations. Unlike point sources, however, individual source data are not stored in NEDS for each small source. Rather, estimates of total emission levels for specific categories of area sources are stored for individual geographic areas.

A summary of emissions by category is given in Tables 4.1 and 4.2. The data shown in Table 4.2 are not reflected in Table 4.1, so amounts shown in Table 4.2 should be added to the grand total shown in Table 4.1.

Table 4.1. EMISSIONS BY CATEGORIES - UNITED STATES

Emission categories	Pollutant, tons per year				
	Particulates	Sulfur oxides	Nitrogen oxides	Hydro-carbons	Carbon monoxide
GRAND TOTAL	**18,566,748**	**32,023,487**	**24,051,210**	**26,632,852**	**101,693,648**
-AREA	**3,891,673**	**4,149,492**	**10,380,875**	**19,803,892**	**82,705,714**
-POINT	**14,675,075**	**27,873,995**	**13,670,335**	**6,828,960**	**18,987,934**
FUEL COMBUSTION-AREA	2,217,301	3,475,451	1,486,484	255,225	668,638
-POINT	5,242,555	21,084,038	10,765,754	217,234	511,267
External Combustion-area	2,217,301	3,475,451	1,486,484	255,225	668,638
-point	5,237,045	21,067,587	9,847,280	173,050	472,428
Residential Fuel-area	299,520	894,519	292,572	137,801	593,634
Anthracite Coal	14,070	36,592	4,221	3,518	126,634
Bituminous Coal	81,291	312,305	12,194	81,291	365,809
Distillate Oil	85,428	479,855	102,514	25,628	42,714
Residual Oil	9,167	62,984	15,942	1,196	80
Natural Gas	51,029	1,611	134,287	21,486	53,715
Wood	58,535	1,171	23,414	4,683	4,683
Electric Generation-point	3,384,726	17,388,406	5,880,746	72,298	234,505
Anthracite Coal	19,420	54,891	13,798	165	3,635
Bituminous Coal	3,223,786	15,554,246	3,852,019	52,535	165,983
Lignite	58,973	107,023	64,311	923	3,122
Residual Oil	52,981	1,579,488	773,377	15,661	23,399
Distillate Oil	2,157	21,210	37,373	673	959
Natural Gas	25,609	19,744	1,104,415	2,089	36,137
Process Gas	590	14,113	31,794	182	788
Coke	460	37,692	3,358	6	187
Solid Waste/Coal	751	0	302	63	295
Other					
Industrial Fuel-area	1,604,488	1,382,156	599,993	79,696	28,204
-point	1,777,004	3,502,676	3,906,712	97,066	230,662
Anthracite Coal-area	106	152	86	1	11
-point	6,208	7,180	3,203	54	1,663
Bituminous Coal-area	1,534,028	1,058,041	202,898	13,527	27,053
-point	1,206,491	2,369,034	545,182	17,513	54,810
Lignite-point	13,239	4,917	3,126	210	421
Residual Oil-area	28,939	273,406	75,492	3,775	252
-point	68,424	841,155	206,827	11,447	13,163
Distillate Oil-area	13,120	49,634	52,479	2,624	175
-point	20,531	39,207	58,629	4,320	5,663
Natural Gas-area	26,839	895	268,386	59,641	596
-point	29,209	36,287	354,160	11,177	28,088
Process Gas-area	6	0	71	12	0
-point	168,923	123,501	2,581,326	13,161	68,525
Coke-point	2,044	24,795	3,003	40	406
Wood-area	1,451	29	580	116	116
-point	211,731	17,555	137,691	30,700	43,838
Liquid Petroleum Gas-point	315	23,388	4,964	132	653
Bagasse-point	41,958	0	5,490	5,499	5,499
Other-point	7,931	15,659	3,109	2,812	7,935
Commercial-Institutional Fuel-area	313,293	1,198,776	591,919	37,727	46,801
-point	75,315	176,505	59,823	3,686	7,261
Anthracite Coal-area	1,428	3,880	1,461	29	877
-point	6,798	2,622	824	51	284
Bituminous Coal-area	154,062	234,544	28,247	6,141	22,108
-point	52,185	82,613	17,158	1,249	3,313
Lignite-point	4,229	2,930	1,015	75	204
Residual Oil-area	67,358	701,296	175,717	8,786	586
-point	7,248	79,949	18,650	884	1,149
Distillate Oil-area	69,237	258,386	276,949	13,847	923
-point	1,024	5,929	4,390	206	285
Natural Gas-area	21,192	669	111,538	8,923	22,308
-point	3,130	2,404	17,088	1,069	1,881
Wood-area	15	0	6	1	1
-point	672	53	656	146	131
Liquid Petroleum Gas-point	14	1	78	6	15
Miscellaneous-point					
Internal Combustion-point	6,510	16,450	918,474	44,184	38,839
Electric Generation	3,519	5,640	51,288	1,527	3,124
Distillate Oil	3,205	4,431	24,114	201	38
Natural Gas	87	554	19,669	159	30
Diesel Fuel	176	356	4,911	699	2,963
Industrial Fuel	2,703	10,565	865,375	41,878	33,776
Distillate Oil	497	842	4,936	202	907
Natural Gas	1,651	9,532	857,712	40,597	28,459
Gasoline	11	5	262	691	2,611
Diesel Fuel	86	167	2,342	249	1,467
Other	458	18	123	138	332
Commercial-Institutional	47	97	1,328	133	808
Diesel Fuel	47	97	1,328	133	808
Other					
Engine-Testing	241	148	482	646	1,132
Aircraft	241	148	482	646	1,132
Other					
Miscellaneous					
INDUSTRIAL PROCESS-POINT	9,265,430	6,753,242	2,876,497	6,450,840	17,469,013
Chemical Manufacturing	225,865	696,367	151,033	2,369,685	6,010,714
Food/Agriculture	401,505	1,659	443	31,602	1,334
Primary Metal	1,691,035	3,637,080	27,787	114,778	4,108,430
Secondary Metals	191,510	103,514	2,925	5,374	1,506,070
Mineral Products	5,211,998	446,210	142,701	11,732	25,316
Petroleum Industry	971,441	1,676,430	2,503,111	979,639	4,888,029
Wood Products	469,852	107,823	2,931	25,477	857,648
Evaporation	1,022	2,120	612	2,774,657	2,149
Metal Fabrication	3,924	1,069	298	1,861	38
Leather Products	59	26	4	418	0
Textile Manufacturing	396	38	18	7,339	1
Inprocess Fuel	87,330	60,496	36,885	22,880	38,092
Other/Not Classified	9,293	20,408	7,750	105,397	31,192
SOLID WASTE DISPOSAL-AREA	717,890	49,287	151,843	1,488,391	3,974,054
-POINT	166,020	36,689	28,084	160,886	1,007,654
Government-point	72,526	9,474	14,597	58,659	213,237
Municipal Incineration	49,780	8,084	6,495	17,472	95,577
Open Burning	22,070	1,346	8,003	40,869	116,348
Other	675	43	98	317	1,312
Residential-area	341,503	11,830	57,141	976,516	2,787,253
On Site Incineration	207,577	3,460	6,919	691,924	2,075,773
Open Burning	133,926	8,370	50,222	284,592	711,480
Commercial-Institutional-area	75,345	7,052	20,446	111,697	263,627
-point	2,951	870	850	1,678	12,610
On Site Incineration-area	37,480	4,685	6,247	31,233	62,466
-point	1,435	869	652	1,323	8,343
Open Burning-area	37,866	2,367	14,200	80,464	201,161
-point	1,442	0	170	339	4,243
Apartment-point	30	1	9	15	24
Other-point	44	0	19	0	0
Industrial-area	301,042	30,406	74,256	400,178	923,174
-point	90,544	26,345	12,638	100,550	781,807
On Site Incineration-area	185,447	23,181	30,908	154,539	309,079
-point	75,489	21,884	9,459	63,214	732,914
Open Burning-area	115,594	7,225	43,348	245,638	614,095
-point	12,900	348	2,939	37,123	48,404
Auto Body Incineration-point	55	0	2	8	42
Other-point	2,099	4,113	238	205	447
Miscellaneous-point					
TRANSPORTATION-AREA	773,643	624,755	8,721,038	16,278,605	77,417,707
Land Vehicles	523,543	508,209	8,515,400	14,613,519	76,005,100
Gasoline	409,020	245,808	6,615,686	14,333,123	74,821,954
Light Vehicles	359,980	215,988	5,159,706	10,981,127	59,529,745
Heavy Vehicles	33,273	19,964	1,109,090	2,262,051	9,320,184
Off Highway	15,768	9,855	346,890	1,089,944	5,972,025
Diesel Fuel	114,523	262,403	1,899,714	280,396	1,183,146
Heavy Vehicles	42,593	85,186	1,206,805	120,681	709,885
Off Highway	18,739	38,919	533,335	53,333	324,325
Rail	53,191	138,297	159,574	106,382	148,935
Aircraft	226,513	45,175	121,615	551,421	975,558
Military	156,563	29,896	75,213	364,265	391,015
Civil	9,501	1,887	8,583	42,079	240,449
Commercial	60,449	13,392	37,819	145,077	344,094
Vessels	23,586	71,371	84,022	102,173	437,050
Bituminous Coal	1,273	3,183	191	1,273	5,729
Diesel Fuel	14,292	37,159	42,876	28,584	40,017
Residual Oil	6,988	30,383	18,230	912	61
Gasoline	1,033	646	22,726	71,405	391,243
Gas Handling Evaporation Loss	0	0	0	1,011,491	0
MISCELLANEOUS-AREA	182,839	0	21,510	1,781,671	645,315
Slash Burning	182,839	0	21,510	215,105	645,315
Solvent Evaporation Loss	0	0	0	1,566,566	0
MISCELLANEOUS-POINT	70	26	0	0	0

Table 4.2. EMISSION FROM MISCELLANEOUS SOURCES

Category	Particulates, tons/yr	SO_x, tons/yr	NO_x, tons/yr	HC, tons/yr	CO, tons/yr
New York point sources	343,000	1,028,000	421,000	140,000	49,000
Forest wild fires	413,00	0	97,000	583,000	3,399,000
Agricultural burning	300,000	16,000	32,000	300,000	1,600,000
Structural fires	57,000	0	7,000	67,000	220,000
Coal refuse fires	110,000	141,000	34,000	68,000	340,000
Total	1,223,000	1,185,000	591,000	1,188,000	5,608,000

4.1.2 Nitrogen Oxides Emissions (NO_x)

4.1.2.1 Stationary Sources--Stationary sources contribute at least half the total man-made nitrogen oxides (NO_x) in the United States. Recent estimates are that over eleven million tons of NO_x were emitted from stationary sources in 1972. Of total stationary source emissions, about 98% result from combustion of fossil fuels. The remainder comes from industrial processes such as the manufacture of nitric acid, sulfuric acid and explosives. Figure 4.1, showing major stationary sources of NO_x emissions, indicates that utility boilers are the major contributors (48%). Utility boilers and stationary internal combustion engines and gas turbines together account for approximately 70% of the total. Industrial steam-raising boilers account for more than 18% of emissions.

As shown in Figure 4.1, the major combustion source categories are utility boilers, industrial boilers, stationary internal combustion engines, gas turbines, commercial and residential heating systems, industrial process furnaces and incinerators. For each of these categories there are sub-categories based on equipment design and these may be further subdivided depending on type of fuel. Stationary combustion processes are fired with a variety of fossil fuels (i.e., coal, heavy oil, light oil and natural gas) dependent on user and equipment design.

The emission inventory being developed for the Control Systems Laboratory (ERC/RTP) has subdivided stationary sources into 138 different categories of equipment design and fuel burned. Rank of sources in general categories appears in Figure 4.1; rank of sources in more detail is shown in Table 4.3, where those accounting for about 70% of total emissions are listed. These leading combustion sources show the very large number of different equipment and fuel combinations and emphasize the complexity of developing NO_x control technology for such varied sources. The two leading sources in Table 4.3 are gas-fired spark ignition stationary I. C. engines (accounting for over 16% of emissions) and bituminous coal-burning tangentially fired utility boilers (accounting for about 12%).

4.1.2.2 Mobile Sources--Oxides of nitrogen form in mobile sources primarily by the fixation of atmospheric nitrogen in the combination process. Peak temperatures found are those most significant in dissociating N_2 atoms. Exhaust gas recirculation (EGR) and water injection schemes are methods to reduce the peak temperature and thus the amount of oxide of nitrogen produced. EGR methodology was employed in 1973 vehicles. It

Table 4.3. ESTIMATED 1972 NO_x EMISSIONS FROM STATIONARY SOURCES
(Partial Listing of Equipment Type and Fuel Burned Accounting for Approximately 70% of Total Emissions)

	Source Category Equipment/Fuel	NO_x Emissions Est. TPY X 10^6	Percent of Total
1.	I. C. Engines, Spark Ignition, Gas Fired	1.873	16.18
2.	Utility Boilers, Tangential Firing, Bituminous Coal	1.388	11.99
3.	Utility Boilers, Cyclone Firing, Bituminous Coal	0.730	6.31
4.	Utility Boilers, Horizontally Opposed Wall Firing, Gas	0.568	4.91
5.	Utility Boilers, Front Wall Firing, Gas	0.393	3.39
6.	Utility Boilers, Horizontally Opposed Wall Firing, Dry Bottom, Bituminous Coal	0.368	3.18
7.	Utility Boilers, Front Wall Firing, Dry Bottom, Bituminous Coal	0.363	3.14
8.	I. C. Engines, Diesel, Oil and Dual Fuels	0.316	2.73
9.	Utility Boilers, Horizontally Opposed Wall Firing, Wet Bottom, Bituminous Coal	0.306	2.64
10.	Utility Boilers, Front Wall Firing, Wet Bottom, Bituminous Coal	0.302	2.61
11.	Utility Boilers, Horizontally Opposed Wall Firing, Residual Oil	0.271	2.34
12.	Utility Boilers, Front Wall Firing, Residual Oil	0.271	2.34
13.	Industrial Boilers, Bent Tube Wall Fired Packaged Watertube, Residual Oil	0.206	1.78
14.	Industrial Boilers, Firetube Wall Fired Package Scotch, Residual Oil	0.192	1.66
15.	Utility Boilers, Tangential Firing, Residual Oil	0.177	1.53
16.	Gas Turbines, Gas Fired	0.172	1.49
17.	Industrial Boilers, Front Wall Fired, Field Erected Watertube, Residual Oil	0.165	1.43
18.	Industrial Boilers, Horizontally Opposed Wall Firing Field Erected Watertube, Residual Oil	0.165	1.43

reduces oxides of nitrogen emissions from 40 to 60% depending on the base year chosen.

Oxides of nitrogen emission factors for vehicles are:

Light-duty vehicles	
pre 1968	3.6 grams per mile
1968	4.3 grams per mile
1969	5.5 grams per mile
1970	5.1 grams per mile
1971-72	4.8 grams per mile
1973-75	2.3 grams per mile
Diesels pre 1975	1.6 grams per mile
Statutory	0.4 grams per mile
Heavy-duty vehicles	
gasoline pre 1970	9.4 grams per mile
1970-73	9.2 grams per mile
Diesels	34 grams per mile
Aircraft (for example, a JT-9D jumbo jet)	
taxi-idle	2.75 kg/hour
take-off	327 kg/hour
climb-out	208 kg/hour
approach	24.5 kg/hour
per landing-take-off cycle	14.2 killograms

The variations seen for aircraft demonstrate the complexity of deriving meaningful factors. Fluctuations of two or three orders of magnitude are common to all mobile source emissions depending upon operating cycles. In light-duty vehicles these fluctuations may occur in seconds or less; for this reason, physical integration of the sample through the constant volume sample is used. This is much more efficacious than mathematical integration. The latter approach must be used to determine nodal emissions as in design research for control devices.

In addition to EGR for light-duty vehicles, reduction catalysts are proposed to attain the statutory limits. These catalysts would be placed prior to the oxidation catalysts immediately after the exhaust manifold. The vehicle would be operated in a reducing mode, somewhat rich. After the reducing catalyst air would be added to the exhaust stream which would then be passed through an oxidizing catalyst. Single bed catalysts have also been proposed. These require precise control of air/fuel ratio in each cylinder and would probably be practical only if automotive fuel injection were used.

Single bed catalysts may have unique properties depending on operating conditions. Usually catalyst temperature is controlled, but one experimental catalyst which showed minimal NO_x emissions on the Federal test cycle could be operated under other conditions which (a) showed almost no NO_x reduction or (b) almost quantitatively reduced the emissions to ammonia.

Review of the statutory limit now under way is the key to future control efforts. The rise of NO_x in light-duty vehicles seen in 1968-69 was one result of cleaner vehicle operation due to hydrocarbon and carbon monoxide controls. A fuel penalty varies with each engine class.

4.1.2.3 Ambient Air Concentration Summary--In 1972, of 24.1 million tons of NO_2 emitted to the atmosphere of the United States, 36% was from transportation and 57% from stationary point sources.

Figures 4.2 and 4.3 present the seasonal diurnal patterns of NO and NO_2, respectively. These curves reveal that NO and NO_2 have markedly different diurnal patterns; NO concentrations follow traffic patterns while NO_2 does not. The quantity of NO_2 builds up throughout the daylight hours, reaching a maximum in the early afternoon around 4:00 p.m. (see Figure 4.3) and then leveling off to a minimum just before sunrise.

Seasonal curves (see Figures 4.3 and 4.4) demonstrate the lower autumn but higher spring and summer NO_2 values. Figure 4.4, which is a composite NO_2 pattern from all six CAMP sites, shows the more consistent summer peaks, especially since 1969.

A long-term trend line for NO_2 is shown in Figure 4.5, which is again a composite graph of the six CAMP sites. It shows a general increase in NO_2 concentration levels at these six sites.

Historically, NO_2 measurements were made in most of the AQCR's by now discredited FRM. According to these data, there were 41 AQCR's which should be classified priority 1. An intense monitoring study was conducted in these 41 AQCR's using the arsenite and chemiluminescent methods. After two years of monitoring in these AQCR's, three cities had yearly averages over 100 $\mu g/m^3$--Chicago, Springfield, Massachusetts and New York City. In addition, Denver, Cincinnati, Philadelphia and Salt Lake City should be carefully watched for a future problem.

As part of the NASN gas network, samples were collected once every 12 days since 1972 at approximately 200 urban and nonurban sites across the U.S. Annual averages from this network show that in 1972 40 sites had concentrations over 100 $\mu g/m^3$, and in 1973 three sites had over 100 $\mu g/m^3$, all located in one AQCR--Metropolitan Los Angeles Intrastate. (Note: Continuous data were also collected in L.A. as part of the CHESS Program. These data also indicate that L.A. is priority 1.)

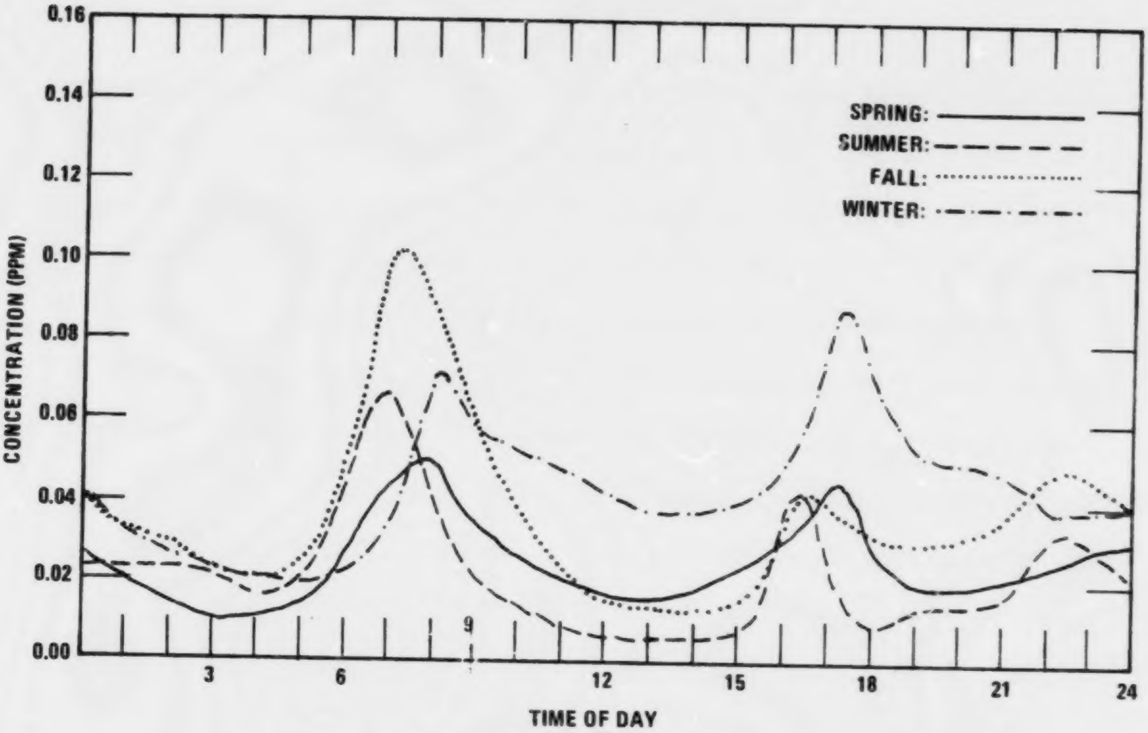

Figure 4.2. Seasonal diurnal patterns of nitric oxide concentrations.

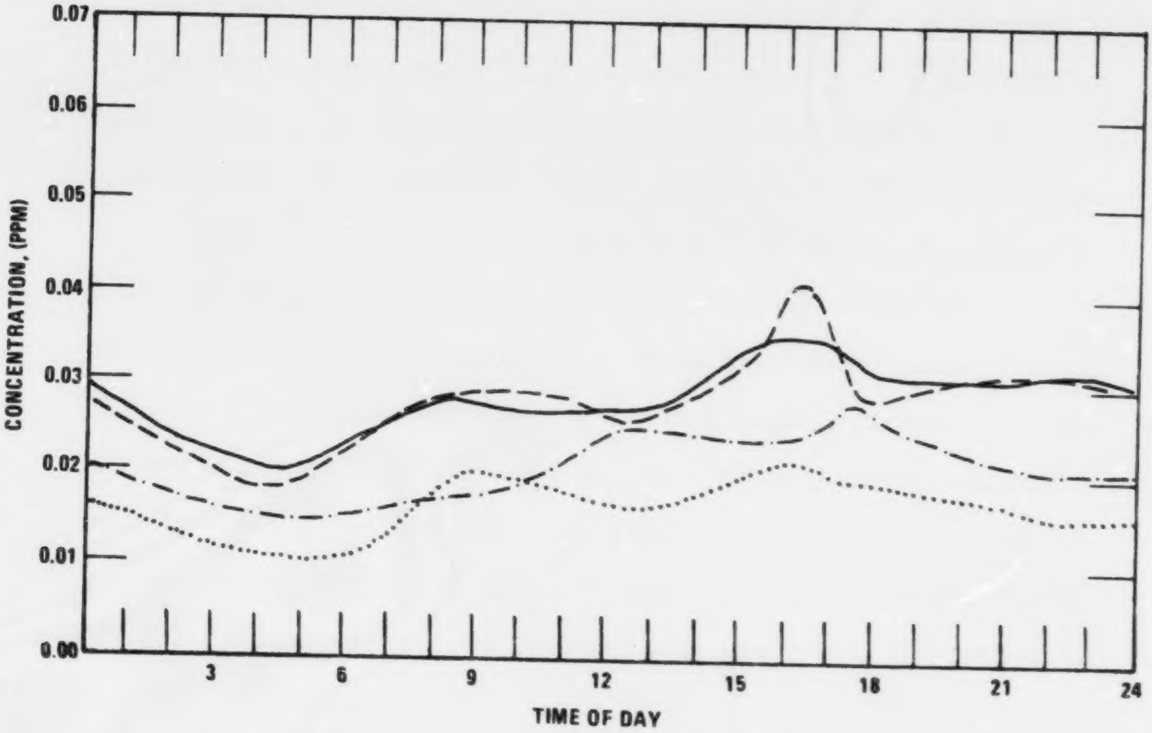

Figure 4.3 Seasonal diurnal patterns of nitrogen dioxide concentrations.

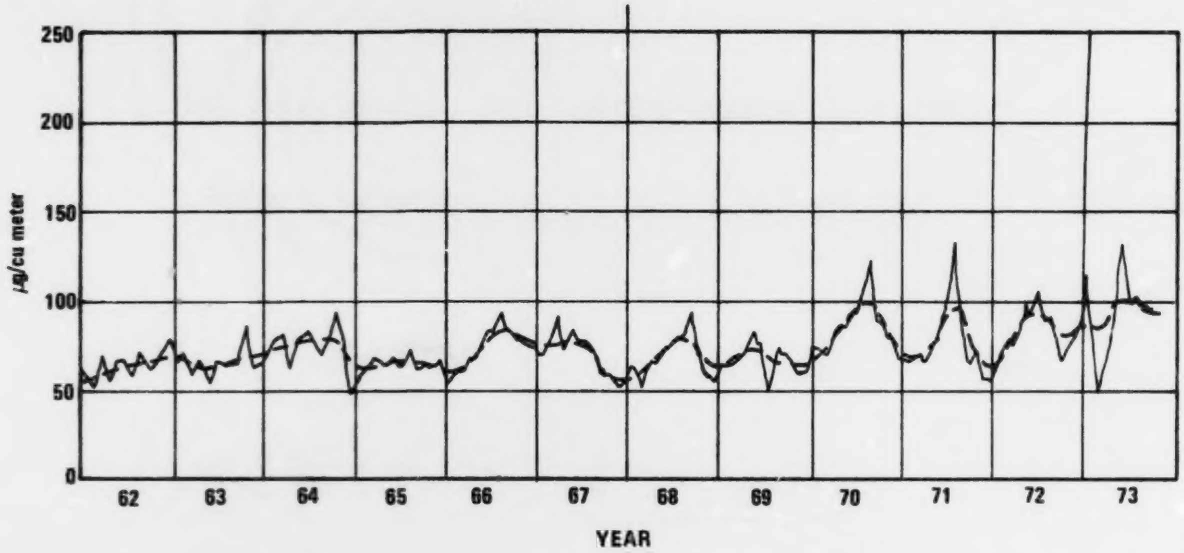

Figure 4.4. Seasonal pattern of nitrogen dioxide concentration levels, composite graph of the six CAMP sites.

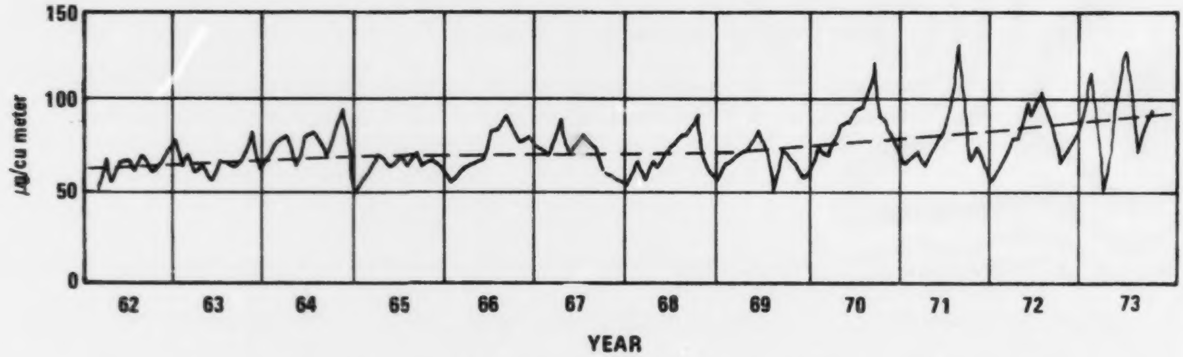

Figure 4.5. Long-term trend line for nitrogen dioxide concentration levels composite graph of the six CAMP sites.

Table 4.4. RECLASSIFICATION STUDY - 24-HOUR DATA

Year	Total No. of Urban Sites	No. of Sites within Interval Concentration Interval, μg/m^3			
		<50	50-74	75-99	>99
1972	129	79	41	5	4
1973	169	78	69	19	3

Year	Total No. of Urban Sites	No. of Sites within Interval Concentration Interval, μg/m^3	
		≤20	>20
1972	22	20	2
1973	29	21	8

We find that NO_2 is essentially an urban problem influenced by local sources (primarily mobile in areas of high levels) and meteorological factors, as indicated by seasonal patterns. In areas with more than one monitoring device, data show that local maximum concentrations do exist where one site is over the standard and others are not in excess of the standard of 100 μg/m^3.

Overall, the NO_2 problem is less severe than we first thought. However, with four areas above the standard and another four near the standard, it remains a problem.

4.1.3 Carbon Monoxide

4.1.3.1 Natural Sources--The primary source of CO in urban atmospheres is incomplete combustion. In the global atmosphere, most carbon monoxide is produced by natural sources from the oxidation of methane by hydroxyl radicals. The same OH radicals account for a large amount of global CO loss. These two competing formation and destruction processes can account for the 0.1 year residence time of CO estimated by radiocarbon measurement. While important in explaining the global balance, oxidation of CO by OH is insignificant in polluted atmospheres, being unable to compete with the much faster reactions of hydrocarbons with OH.

Evidence suggests that large amounts of CO are produced through reaction of methane in the troposphere. The oxidation of CH_4 by hydroxyl radicals liberates CH_3 radicals that can later undergo reaction to form CO. McConnell, et al.[1] estimated a substantial rate of CO production from the reaction of CH_4 and OH. They concluded that while combustion sources determine local levels of CO, the natural sources determine the global level, with the oxidation of methane playing a leading role. From an analysis of radioactive CO data in the troposphere, Weinstock and Niki[2] concluded that CO is produced at a rate 25 times greater than that of CO formation from combustion. Based on their measurements, they calculated the rate of CO formation from the reaction of CH_4 and OH. The value they derived is of the same order of magnitude as that extimated by McConnell et al., lending support to this view.

Levy[3] recently developed a model showing that sufficient global concentrations of water vapor, CH_4, O_3 and NO_x exist to cause chain reactions that can destroy CO as well as produce it. He calculated that the hydroxyl radicals produced in chain processes can oxidize CO at a rate in excess of the rate of CO production from the reaction of CH_4 with OH. His model predicts that competing formation and destruction processes result in a residence time of 0.1 year for CO, agreeing with the Weinstock[4] estimate deduced from radiocarbon measurements.

4.1.3.2 Mobile Sources--With the start of the 1975 model year, many new cars were equipped with oxidation catalyst-converters for reducing emission levels of both CO and hydrocarbons. Preliminary results on prototype 1975 cars available at this laboratory indicate three to seven times lower CO emission levels for catalyst-equipped cars over equivalent 1973 and 1975 cars and better than 10-fold improvement over 1972 cars. The 1975 prototype vehicles evaluated are in some cases considerably different from production vehicles actually being sold. One manufacturer uses the catalyst with only one bank of cylinders.[4]

Another method to reduce CO and other harmful exhaust gas components is the new engine design using the stratified charge concept for combustion in a two-chamber engine. Reported values for the only stratified-charge equipped car commercially available, Nonda CVCC, show it meeting the 1977 emission standards for CO and hydrocarbons without extra treatment of exhaust gas. CO emission levels are about 2 gm/mi for all commercially available engine sizes of the Honda.

One complication in achieving the ambient air quality standard for CO by controlling auto exhaust emission is the effect that temperature has on emission rates for both CO and hydrocarbons. This was first reported by R. W. Hurn of the U.S. Bureau of Mines[5], who found it to exist in six 1973-73-74 catalyst-equipped cars. Comparing relative emissions for the three regulated species at ambient temperatures from 20°F to 110°F, it was found that CO and hydrocarbon emission increased up to six times at the lowest temperature compared to the normal Federal Test Procedure temperature range of 70-75°F. There was no significant change in NO_x emissions, however.

Other work has also shown higher emission levels at higher temperatures, so that tests under defined ambient conditions represent a minimum case. The importance of these findings is that while new model cars may meet the emission standard as measured by the Federal Test Procedure, actual operation of these catalyst-equipped cars at sites of different temperature or in early morning could produce unexpected higher emission rates for CO and hydrocarbons. We need to know more about causes and extent of departures from standard conditions; the Federal Test Procedure should be capable of detecting emissions in all possible operating conditions and environments.

4.1.4 Hydrocarbons

4.1.4.1 Mobile Sources--The Clean Air Act specifies a 90% rollback on hydrocarbon emissions from 1970 levels for light-duty vehicles.

Standards are:

Pre-1968	8.6 estimated	grams/mile
1973-74	3.0	grams/mile
1975 US	1.5	grams/mile
1975 Calif.	0.9	grams/mile
1976	0.41	grams/mile

Due to the complexity of hydrocarbon mixture emitted from light-duty vehicles, control of total emissions was adequate. Minor variations in composition did not seriously effect the total. Catalytic controls strongly enhance some materials like methane which is much more stable and has a profound effect on relative reactivity of total emissions. Non-catalytically-controlled vehicles produce less than 10% methane. Acetylene is also significant. In catalytic vehicles higher molecular weight species are preferentially oxidized and methane may account for 30 to 40% of total emissions. In specific operating modes, as much as 80% of hydrocarbons may be methane.

The N.A.S. report has supports current standards, but only if other mobile sources conform to similar controls.

As is discussed in Section 3, hydrocarbon emissions vary with cycle and operating conditions. Emission factors and regulations try to integrate these emissions into numbers which can be related (through number of vehicles) to impact of specific source on the environment.

A compilation of these factors by an average use cycle is given in AP-42 compilation of Emission Factors, Supplement 2.

Current in-house tests show prototype vehicles* emit:

Ford	0.20 ± .02 gm/mi
Plymouth	0.23 ± .03 gm/mi
GM	0.44 ± .03 gm/mi

4.1.5 Sulfur Oxides

4.1.5.1 Mobile Sources--Trace quantities of sulfur mostly in the form of organic compounds are present in gasoline (0.038%). Combustion of gasoline in an automotive engine yields principally carbon dioxide (CO_2) and water along with hydrocarbons (HC), carbon monoxide (CO), nitrogen oxides (NO_x), sulfur dioxide (SO_2) and sulfur trioxide (SO_3). During normal combustion, sulfur in gasoline is almost all converted to SO_2 and SO_3 with the latter accounting for less than 2% of all sulfur. The SO_3 reacts very rapidly with water in the exhaust and is emitted as sulfuric acid or sulfate particulate.

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*These data cover emissions from one vehicle from each manufacturer.

The amount of SO_2 and SO_3 emissions from mobile sources nationwide is negligible (less than 1%) compared with that from stationary sources. For this reason they are not a significant portion of overall sulfur oxides air pollution except in a few places like Los Angeles, where stationary source emissions of sulfur oxides are relatively low.

It was recently reported and has since been confirmed that cars with catalytic converters emit substantial amounts of sulfuric acid. Conversion of 40% of the fuel sulfur has been reported. In the absence of the catalytic converter, conversion is less than 2% of the fuel sulfur.

Although the contribution of mobile sources to total regional airborne sulfate is not significant, use of catalytic converters as presently designed may result in localized buildup of sulfuric acid and sulfate salts concentrations to dangerous levels, especially near places like Southern California where the sulfur content of gasoline is higher than the national average. Because health problems may result from direct emissions of substantial amounts of sulfuric acid mist by catalyst-equipped cars, EPA is reassessing the automotive sulfur oxide emission question.

4.2 TRANSFORMATION AND TRANSPORT

4.2.1 Oxides of Nitrogen

In the laboratory, investigators have been able to account for over 90% of carbon atoms; however, only 50% of the nitrogen could be accounted for in many cases. Apparently most of the unaccounted nitrogen atoms end up as nitric acid either on the walls of the reactor or in the gas phase.[6,7] Recent investigations suggest that nitric acid is also produced in atmospheric photolytic processes.[8]

Nitric acid in the gaseous state is colorless and photochemically stable. It is volatile acid in solution. The equilibrium vapor pressure decreases with increasing dilution and at the parts-per-hundred-million level--as might be expected in the atmosphere--the solution would be extremely dilute. In the atmosphere, nitric acid can be produced by two reactions:

(1) $OH + NO_2 \xrightarrow{M} HNO_3$

(2) $N_2O_5 + H_2O \rightarrow 2HNO_3$

Nicolet[9] has postulated reaction (1) for the presence of nitric acid in the stratosphere. Gay and Bufalini[6] have postulated reaction (2) for the formation of nitric acid in smog chambers. It is not known which reaction is most important in polluted atmospheres. Good nitrogen balances have been obtained in smog chamber studies when nitric acid is included as a product.[6,7]

Nitrous acid is not formed in as great quantities as nitric acid. It can be produced in the atmosphere by the reaction,

$$NO + NO_2 + H_2O \rightarrow 2HNO_2$$

This acid is important because of its photochemical reactivity. Nitrous acid absorbs sunlight and dissociates into OH and NO. Its photolysis rate is lower than the photolysis of NO_2, but in photochemical smog production it produces very reactive hydroxyl radicals when photodissociated.

Although strategy to alleviate NO_x-related pollution is in existence, the transformation of NO_x in ambient air is still at issue. The "NO_x issue" consists of the following partly answered or unanswered questions:

- What are the products of atmospheric reactions of NO_x and what determines accumulation levels?

- What is the quantitative dependence of NO_2 on NO_x and on other possible precursors?
- What is the role of NO_x in the atmospheric oxidant formation process? Should NO_x control be included in oxidant control strategy?

EPA is currently conducting laboratory and field studies to develop analytical methods for measurement of the atmospheric reaction products of NO_x.

Present NO_2 control strategy assumed NO_x to be the sole precursor of NO_2 and to yield NO_2 on a 1:1 basis. This, however, is only a simplifying approximation. Although NO_2 is a product of the thermal reaction of NO_x with atmospheric oxygen, this reaction alone cannot cause the observed accumulations of NO_2 in ambient air. Such accumulation is caused by a photochemical process that involves both NO_x and HC as reactants.

Smog chamber testing of simulated atmospheric mixtures has shown that maxiumum NO_2 concentration during the test is proportional--in fact, almost equal--to the initial concentration of NO_x and nearly independent of the initial HC concentration (Figure 4.6). However, unlike the maximum NO_2, average NO_2 concentration during the test was found to depend on both NO_x and HC. The average NO_2 increased with increasing initial NO_x but decreased with increasing initial HC (Figure 4.7).

The aerometric data analysis done thus far verified the 1:1 relationship between the early-in-the-morning (6-9 a.m.) NO_x and the later-in-the-day NO_2 maximum (Figure 4.8), but failed to establish the dependence of the average NO_2 on both (the NO_x and HC) precursors.

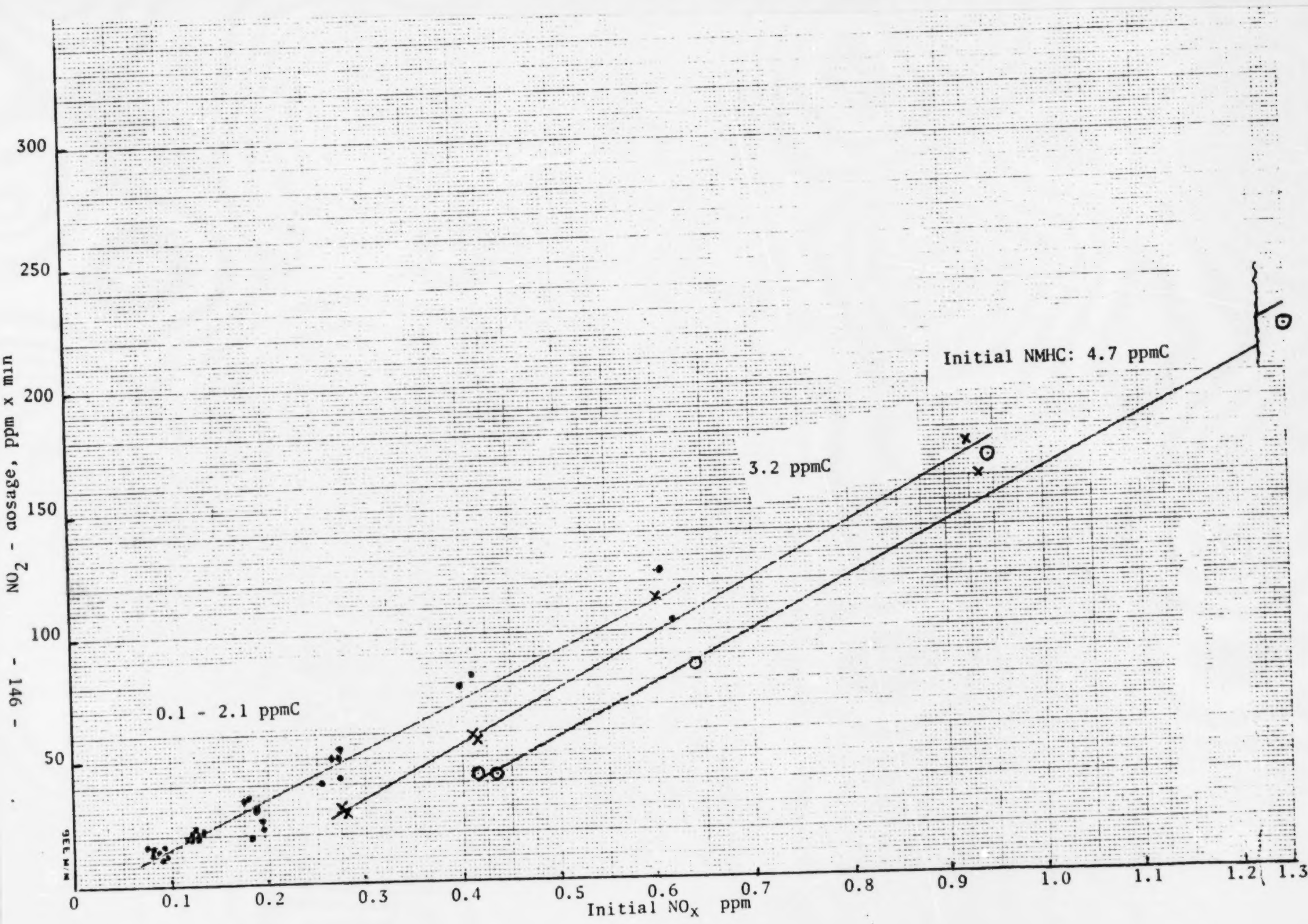

Figure 4.7. Nitrogen dioxide dosage as a function of initial NO$_x$ at various initial NMHC levels (Smog chamber data)

It appears that the daily maximum NO_2 concentration relates to the NO_2 precursors simply; namely, it is proportional to the daily 6-9 a.m. NO_x and is independent of HC. Unlike the daily maximum, the daily average NO_2 is neither simply nor predictably related to the NO_2 pre cursors; this makes it difficult to determine control requirements for NO_2, because the NO_2-NAQS is defined in terms of an (annual) average NO_2 concentration.

To determine control requirements for achievement of NO_2 standards, one must consider that the yearly average concentration of NO_2 in a region results from combined effects of the following processes:

- Photochemical conversion of the morning-traffic-peak NO_x into NO_2, occurring only during daytime.
- Thermal conversion of the morning- and afternoon-traffic-peak NO_x into NO_2.
- Reaction of the afternoon-traffic-peak NO_x with oxidant.

The "photochemical" NO_2--the largest contributor to the annual NO_2--depends on the 6-9 a.m. NO_x and possibly on the 6-9 a.m. HC also. More aerometric and smog chamber data are needed here for accurately determining dependence of the average NO_2 on initial (or early-in-the-morning) levels of NO_x and HC.

The "thermal" NO_2 depends strongly and predictably on NO_x so that it could be controlled effectively by NO_x control. However, thermal NO_2 does not contribute to annual NO_2 in a major way.

The "evening" NO_2, resulting from the O_2-NO_x reaction, appears to depend mainly on the oxidant level. Therefore, the most effective means for controlling such NO_2 to the 24-hour NO_2 average has not been

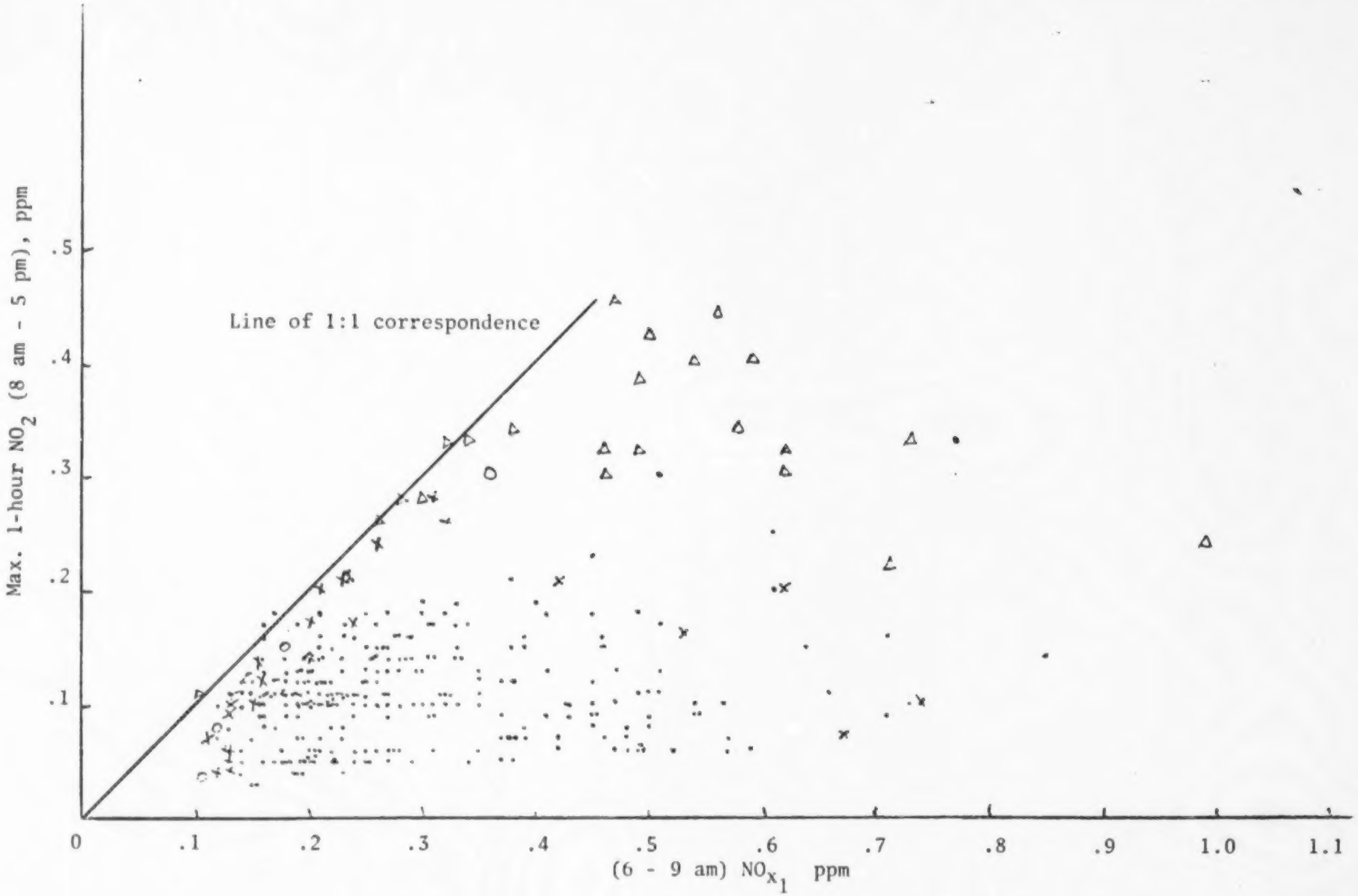

Figure 4.8 Correlation of aerometric data on NO_x (6-9 am) and maximum - 1-hour-NO_2 (8 am - 5 pm). (Data from all CAMP Cities)

established. However, it has been significant, especially during the smog season. Analysis of aerometric data is needed here to establish the importance of such NO_2, within and outside the smog season, and to determine its dependence on the oxidant and NO_x levels. Since present photochemical pollution control strategies aim at reducing oxidant to 0.08 ppm, one could reasonably assume that evening NO_2 is decreasing and will eventually become negligible.

Smog chamber studies have shown that both HC and NO_x have a role in the atmospheric oxidant formation process. They have shown the oxidant to increase with increasing HC reactant, and to show a maximum dependence on NO_x. Aerometric data similarly showed the oxidant to increase with increasing concentrations of HC reactant but were not sufficiently abundant to permit delineation of both HC and NO_x effects. Based on this data, an oxidant control strategy calling for unilateral control of HC emissions but overlooking the role of NO_x may not be the most effective.

Present oxidant control strategy is based on empirical correlation of ambient oxidant and HC concentration data that shows the daily oxidant to decrease with decreasing 6-9 a.m. HC concentration (Figure 4.9). Unfortunately, there is insufficient data to establish the correlative dependence of oxidant on NO_x. There is evidence to suggest, however, that the NO_x effect is an inhibitive one, and that as ambient HC levels decrease with control, the NO_x-to-HC ratio increases and the inhibitive effect of NO_x is intensified. According to this evidence, ignoring the NO_x effect unavoidably leads to an overestimation of HC control requirements.

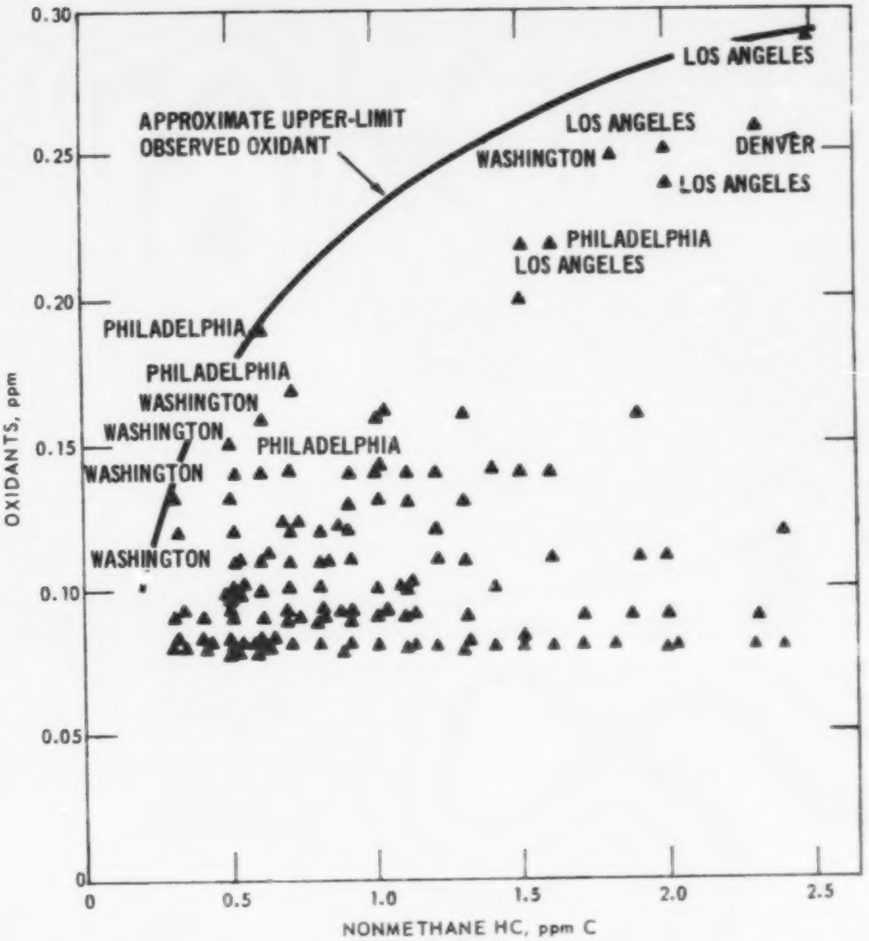

Figure 4-2. Maximum daily 1-hour-average oxidants as a function of 6-to 9-a.m. averages of nonmethane hydrocarbons at CAMP stations, June through September, 1966 through 1968, Los Angeles, May through October 1967.

Hypothetical oxidant control strategy considering the NO_x role should be expected to call for less HC control. Such a hypothetical strategy is not possible simply because, as yet, no one has been able to quantitate the role of NO_x. Aerometric data are not complete enough to permit such quantification. Smog chamber data are more complete; however, such data do not necessarily represent ambient atmospheric conditions. This hypothetical strategy may have merit in an urban region, but its effectiveness in controlling "transported oxidant" buildup in rural areas downwind from cities is questionable.

4.2.2 Carbon Monoxide

The oxidation of CO by hydroxyl radicals

$$CO + OH \rightarrow CO_2 + H$$

is rapid enough to suggest that this reaction might be a significant removal process for CO in polluted atmospheres. It was recently determined, however that the reaction cannot compete effectively with the much faster reactions of hydroxyl radicals with hydrocarbons.[10,11] In the absence of reactive hydrocarbons, modeling studies predict that OH is an effective sink for CO.[12] Subsequent chain reactions are effective in converting NO to NO_2 and small amounts of O_3 an be formed, although under non-urban conditions, not enough to exceed the air quality standards. No significant oxidation reaction of CO has yet to be found for urban atmospheres. The reaction of CO with HO_2

$$CO + HO_2 \rightarrow CO_2 + OH$$

was though to be an atmospheric reaction of possible importance, but this reaction is extremely slow.

4.2.3 Hydrocarbons

New findings on pollutant transport and hydrocarbon reactivity suggested that organics formerly classified unreactive actually may be reactive. Based on these findings, a new classification of organics was derived and the use of reactivity criteria was reexamined. developments prompting this reexamination include:

- Reactivity criteria used inconsistently in existing control regulations.
- Recent smog chamber studies have improved our understanding of the photochemical reactivities of organic compounds and raised questions as to the validity of the reactivity classification in the widely used Los Angeles County Rule 66.
- It has become increasingly evident that pollutant transport does occur, and that such transport enhances formation of oxidant from low reactivity organics.
- The present emphasis on control of mobile source emissions may eventually make solvents and other stationary source emissions the predominant emission problem.

The Los Angeles County "Rule 66" is lacking in two respects. First, its reactivity classification of organics is inaccurate, the error being in the direction of less stringent control. Second, it assumes that organics of unknown reactivity are non-reactive--an assumption that is probably wrong and that again leads to less stringent control. EPA Appendix B is lacking in that it assumes that all except very few organics are equally reactive--an assumption that is known to be wrong and that causes inflexibility.

Recent findings concerning pollutant transport provide additional support for the "all-organics" control concept. Thus, under prolonged irradation conditions occurring in transported air masses, it is very probably that the "less reactive" organics are induced to form as much oxidant as the "more reactive" ones. Therefore, to alleviate the downwind area, nearly universal control of organics probably would be more effective than the more selective control prescribed by Rule 66.

Control requirements for each source should include consideration of: (a) the degree of total hydrocarbon control required for the region or area; (b) the relative strength of the source; (c) the reactivity of the emissions, and (d) the availability of control technology.

A new reactivity classification of organics based on existing smog chamber reactivity data has been derived. The new classification categorizes hydrocarbon and non-hydrocarbon organics into five reactivity classes and gives a numerical reactivity rating to each class.

4.2.4 Oxidant

Dependence of the atmospheric oxidant on ambient levels of hydrocarbon and NO_x has been explored in laboratory (smog chamber) as well as field studies. Early laboratory studies had little success--mainly because atmospheric conditions could not be closely simulated in the smog chamber. The oxidant - HC - NO_x relationships from those studies have only qualitative validity. Aerometric data gave a somewhat more valid, but considerably less complete, relationship--namely, a correlative dependence of oxidant on HC alone. The dependence on both HC and NO_x could not be obtained.

Recent smog chamber studies have used improved methodology and experimental conditions much closer to those occurring in the real atmosphere. Their results, therefore, are more valid than those of earlier studies. The most significant deductions from these recent studies are that: (1) oxidant concentrations exceeding the standard (0.08 ppm-O_3) can form from only a few parts-per-hundred-million of hydrocarbon, and (2) the oxidant level within an urban area can be kept below the standard by maintaining the early-in-the-morning HC-to-NO_x ratio at 2.5:1 or less.

Nevertheless, the question of comparability of smog chamber atmosphere remains open, and the validity of these or any other smog chamber data cannot be fully defended at this time.

Some recent studies suggest that ozone and ozone precursors can be transported over long distances. Concentrations of ozone are found in remote areas that frequently exceed the air quality standard. The probable cause for these high ozone levels has been hypothesized to be long-range transport. Present evidence is insufficient to implicate natural sources as major contributors, although the possibility cannot be ruled out.

4.2.5 Particulate

Since the original criteria document was issued, major advances have been made in understanding the sources, properties, chemical composition and dynamics of the atmospheric aerosol or total suspended particulate matter.

Current problems are examined in ERC-RTP Task Force documents: Summary Report on Suspended Sulfates and Sulfuric Acid Aerosol and

Briefing Report on Problems Relating to Fine Suspended Particulates. The National Academy of Sciences has prepared a review, now in draft, as background for preparation of a new criteria document. Therefore, in this document only a few key references are discussed. While no decisions have been made, it is clear that both particle size and particle composition must be considered and that in addition to primary aerosols, gaseous precursors of secondary aerosol (aerosol formed by chemical processes in the atmosphere) must be controlled. These include SO_2 (forms of sulfate aerosol), NO_x (forms nitrate aerosol) and certain organic vapors (from organic aerosol).

Key areas of progress include:

(1.) Understanding the multimodal distribution of the atmospheric aerosol, the typical observation of a bimodal mass-size distribution, and the differences in chemical composition and effects of fine and coarse aerosols.

(2.) Use of microscopy and the chemical element balance technique to determine aerosol source coefficients from measurements of ambient aerosols. This has led to the realization that secondary sulfate, nitrate and organic aerosol comprise most fine particulate matter and that in urban areas, road dust, tire debris and other material generated by vehicular traffic make a major contribution to coarse particles.

(3.) Identification of organic material as a major primary and secondary component of fine particulate matter, and determination of the chemical composition of many individual organic compounds in the atmospheric aerosol.

(4.) Realization of the regional nature of sulfate pollution, identification of several compounds including acid sulfates in the atmosphere, improved understanding of the coversion of SO_2 to sulfate and measurements of transformation rates in power plant plumes and urban atmospheres.

(5.) Development of improved instruments and techniques for measuring aerosol parameters important in visibility reduction, radiation balance and weather and climate modification.

4.2.5.1 Distribution of Aerosol and Chemical Composition as a Function of Size-Distribution--Early studies of ambient particulate matter used five-stage impactors and found that the size distribution could be adequately accounted for by a log-normal distribution.[13] However, in recent years counting techniques and eight-stage impactor studies have demonstrated a bimodal size distribution in some locations. In the fall of 1973, three separate studies confirmed a bimodal mass distribution and review of counting studies indicated a bimodal volume distribution for almost all measurements.[14-16]

Most aerosol scientists agree that atmospheric particulate matter is multimodal with a variety of particles from different sources having different properties. It is a convenient hypothesis to consider particulate matter as being composed of two distinct size classes, fine and coarse, and such a hypothesis has both an experimental and a theoretical basis.

There are two mechanisms for creating new particles in the atmosphere. Nucleation and gas-particle conversion produce very small particles which grow by coagulation and condensation. As these small particles become larger, the growth processes slow down and virtually cease as the diameter approaches one micron. Comminution or mechanical processes such as breaking condensed matter into smaller particles by grinding, rubbing, etc., produce particles with a mass mean diameter much greater than one micron. The resulting atmospheric distribution in terms of number, surface and volume is shown in Figure 4.10. The lower mode may be called the optical mode since it covers the size range most effective in scattering light, or the accumulation mode since smaller particles grow into this size range. Particles in the lower mode are also within the respirable size range.

4.2.5.2 Composition and Concentration--Although the concentration distribution of fine and coarse particles in the ambient air has not been adequately measured, considerable information about the fine particulate mode can be obtained by observing composition as a function of impactor stage. Most comes from the National Air Surveillance Cascade Impactor Network.[13] Other data have been obtained by research groups.[16] These data indicate that among metals, Pb and V are found primarily in the fine particle mode; Fe, Mg, Mn, Ba, Cd and Cr are found primarily in the coarse particle mode. $SO_4^=$, NO_3^-, Carbon, Cl, NH_4^+ and organic particulate are found in the fine particle mode and $PO_4^=$ in the large particle mode. Zn, Cu, Ni and Sn do not fall clearly in either mode. The data are sparse and limited to a few locations.

Where complete analyses of atmospheric particles have been made (in a limited number of locations), fine particles comprise 25-6-% of the total suspended particulate matter, and from 60 to 80% of the fine particles are secondary.[14,17]

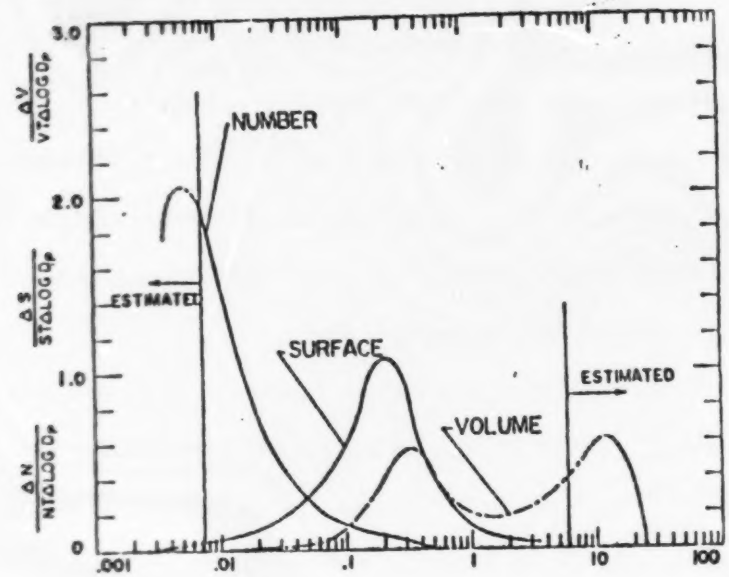

Figure 4.10. Number, surface area, and volume distributions of a hypothetical smog. The linear ordinate normalized by total number, area, or volume is used so that the apparent area under the curves is proportional to the quantity in that size range.

4.2.5.3 Determination of Aerosol Source Coefficients from Ambient Air Sampling and Analysis--Combined chemical, physical and microscopic analysis of collected aerosol is a powerful tool for the identification and quantification of aerosol sources. Aerosol emission inventories are source-oriented, giving primary, anthropogenic emissions only. Inventory information is in mass of particulate material with no size or chemical composition. Aerosol source coefficients are receptor-oriented and express various source contributions to the total ambient aerosol at the point of measurement. Instead of primary anthropogenic emissions only, natural sources, secondary aerosol and unanticipated sources (such as roadway dust) are included.

Source coefficients are useful for providing quantitative information on potential improvement in local aerosol concentrations that would result from either partial or total elimination of emissions from particular sources. Also, they emphasize the substantial contributions to urban aerosols from natural and secondary sources.

The technique of calculating source coefficients from measurements of tamospheric aerosol concentrations and chemical composition was developed by Friedlander.[18] It has been applied to Pasadena, California, by Miler et al.,[19] Friedlander[20] to Chicago, and St. Louis by Gatz.[21]

This technique can be combined with a simple meteorological model to give areawide emission rates of various individual elements.[21] When size-differentiated measurements are available, additional information is obtained for a better estimate of health effects and visibility reduction.[22]

Friedlander's[18] results for Pasadena are shown in Table 4.5.

Data from several other cities show that secondary sulfate, nitrate and organic aerosol contribute 60-80% of fine (< 2 micron diameter) particles and that the fine particulate component varies from 25-60% of the total suspended particulate. The contribution of some secondary components to total suspended particulate matter is shown in Table 4.6.

Table 4.5. ESTIMATED CONCENTRATIONS OF LOS ANGELES AEROSOL PARTICLES BY SOURCE[18]
(Annual Average, 1966)

Source	Mass Concentration ($\mu g/m^3$)
Natural background	
PRIMARY	
Dust rise by wind	8-20
Sea salt	3
Spores, pollen, etc.	Unknown
SECONDARY	
Vegetation (organic vapors)	3-6
Biological (soil bacterial action, decay of organics) NH_3, NO_1, S..	0-7
Man-made	
PRIMARY	
Motor vehicles	15
Organic solvent usage	6
Petroleum	1.3
Aircraft	4
Combustion of fuels	5
Other	5
SECONDARY	
Organic*	11
NO_1^-	13.5
SO_4^{2-}	14.4
Total accounted for	90-105
Measured total	119

*Benzene soluble organic material. This is probably low because some oxidized organic material may be insoluble in benzene.

Table 4.6. PARTICULATE POLLUTION INCLUDING CONSTITUENTS LARGELY OF SECONDARY ORIGIN

	Annual Geometric Mean $\mu g/m$				
City	Total	SO_4^{2-}	NO_{3-}	Org*	NH_4
Boston	93	6.0	1.0	--	1.3
Chicago Site 01	112	10.7	--	7.4	0.8
Detroit	134	12.5	3.5	7.4	0.5
Los Angeles	129	10.8	7.7	15.0	0.8
New York	118	18.6	--	9.3	--
Philadelphia	112	18.4	2.1	8.5	1.8
Pittsburgh	161	14.2	2.5	9.3	0.8
San Francisco	84	7.6	2.9	7.7	0.2

Source: EPA

*Benzene soluble organic material. This includes some primary aerosol but is probably low because some iodized organic material may be insoluble in benzene.

A substantial fraction of coarse particulates in urban areas can be attributed to vehicular traffic-tailpipe emissions, rubber tire dust and mineral fragments. In areas with unpaved roads or parking lots, very large amounts of road dust are generated.[23] Road surfacing and street cleaning are effective control techniques.

4.2.5.4 Organic Aerosol--It has been discovered that organic particulate matter contributes more to total particulate matter than previously indicated by benzene-soluble measurements. Especially during photochemical smog are highly oxidized, polar organic compounds formed which are insoluble in benzene. Studies using more polar solvents have shown that the percentage of organic matter in total suspended particulate in Pasadena, California, averaged 30-40% and varied from 5 to 60%.[24] O'Brien, et al.[25] studied the organic fraction in suspended particle matter collected at several California sites. Benzene soluble varied from 1-12% and averaged 4%; additional organic material extracted by an alcohol mixture varied from 10-42% and averaged 23%. Less extensive studies in Columbus, Ohio, New York City and Pomona, California, gave an average of 36% and a range of 16-56%.[26]

Field and laboratory studies have been conducted to determine the chemical composition of the organic fraction. Model aerosols have been generated from individual hydrocarbon precursors-toluene, alpha-pinene, cyclohexene, and 1-heptene and nitrogen oxides under simulated atmospheric conditions in a 17.3 m^3 environmental chamber. Aerosols were collected on glass-fiber filters and organic matter was obtained by solvent extraction. Organic reaction products were fractionated into acid, neutral, and basic components, and were analyzed by techniques including gas chromatography and gas chromatography combined with mass spectrometry. Different polyfunctional reaction products were identified, including alcohols, aldehydes, ketones, mono- and dicarboxylic acids, and phenols. Tentative identification was made of nitrogen-containing products including nitrate esters and aromatic nitro compounds.[17]

Computer-controlled high resolution mass spectroscopy was used to identify organic compounds in ambient air samples collected in Pasadena and St. Louis. Several hundred different compounds can be identified based on their mass spectrum and time of volatilization from the heated sample.[27] The diurnal variation in aerosol composition has been studied for two size ranges (less and greater than 2 μm) and used to postulate primary and secondary origins of the aerosol. The primary organic aerosols included alkyl benzenes, alkanes, polycyclic aromatics and phenols. Secondary organic aerosols included acids, aldehydes, alcohols, chlorides and nitrates.[28]

Laboratory studies of aerosol generation have shown that aromatic compounds and cyclic olefins are very effective in producing organic aerosol.[29] The aerosol-forming reactivity of various hydrocarbon compounds is shown in Table 4.7.

It has been suggested that some or all of the reported organic aerosol may be organic vapors adsorbed on the fiberglass filter. Hanst, et al.[30] measured HCHO, HCOOH and PAN on one of the days that Friedlander measured organic aerosol. There was as much carbon in these gaseous pollutants as in the organic aerosol. Hanst has suggested that some of the material reported as organic aerosol may have been absorbed HCHO and HCOOH and absorbed decomposition products of PAN.

4.2.6 Sulfur Oxides and Aerosols

4.2.6.1 Laboratory Investigations

4.2.6.1.1 Photochemical and Chemical Oxidation--Chemical mechanisms transforming SO_2 in the atmosphere are still not well known. Oxidation

Table 4.7. AEROSOL AND OXIDANT REACTIVITY OF HYDROCARBONS[29]

Hydrocarbon	Aerosol, b-scat x 10^{-4} m^{-1}			Oxidant, ppm	
	Max	Avg	Category[(a)]	Max	Category[(b)]
Hexanal	0	0	1	0.15	2
Isooctane	0.16	0.08	1	0.08	1
Butane	0.37	0.18	1	--	1
2-Methylbutane	0.79	0.21	1	0.05	1
1-Butene	0.39	0.32	1	0.45	3
Ethylene	0.68	0.34	1	0.46	3
Cyclohexane	1.4	0.45	1	0.10	2
2-Methyl-2-butene	1.1	0.84	1	0.12	2
1-Pentene	1.1	0.89	1	0.37	2
1-Heptene	7.7	2.1	2	0.17	2
Toluene	11.1	2.8	2	0.37	2
Mesitylene	5.7	3.0	2	0.65	3
Benzene	17.0	3.5	2	0.06	1
3-Heptene	4.2	3.8	2	0.41	3
n-Butylbenzene	15.8	7.2	3	0.10	2
o-Diethylbenzene	18.2	7.6	3	0.22	2
t-Butylbenzene	20.8	7.9	3	0.04	1
m-Xylene	13.7	9.5	3	0.36	2
Cyclohexene	36.4	32.4	3	0.41	3

(a)

Category	Aerosol[(b)]	Oxidant
1	<1.3	<0.1
2	1.3-4.0	0.1-0.4
3	>4.0	>0.4

(b) Category based on average aerosol.

by photochemically generated intermediates and catalytic oxidation are now thought the most likely mechanisms.

Laboratory investigations of the photochemical oxidation of sulfur dioxide in air--alone and in the presence of nitrogen oxides and hydrocarbons--indicate that the homogeneous reaction of electronically excited sulfur dioxide ($^3SO_2$) cannot account for the observed oxidation rate of SO_2 in the atmosphere. Current belief is that reactive intermediates formed in the hydrocarbon-NO_x photochemical system are reacting with ground state molecules of SO_2 to form products. These products are thought to account for the homogeneous formation of SO_3 and sulfuric acid mist. Swedish and U.S. workers have identified acid aerosol (H_2SO_4 and/or NH_4HSO_4), $(NH_4)_2SO_4$, $(NH_4)_3H(SO_4)_2$ and $CaSO_4$ in atmospheric samples.[31,32]

$O + SO_2$

The three-body oxidation of SO_2 + O atoms has been postulated to explain the conversion of SO_2.[33] However, the recent evaluation of the rate constant by Davis[34] with N_2 as the third body has shown the reaction to be almost four times slower than previously thought. Thus, this reaction is of only minor importance under most conditions.

$HO_x + SO_2$

Wood, et al.[35] recently conducted a series of photochemical experiments to measure the kinetics of the SO_2 reaction with OH. Their data were interpreted according to the following mechanism:

$$OH + SO_2 \rightarrow HSO_3{}^*$$
$$HSO_3 + M \rightarrow HSO_3$$
$$HSO_3 + OH \rightarrow \text{products}$$

A rate constant of 5.6×10^2 ppm^{-1} min^{-1} for the OH + SO_2 reaction was obtained. Depending on the altitude and presence of pollution sources, OH concentrations between 10^6 and 10^8 molecules/cm^3 have been predicted.[36] Assuming SO_2 = 1 ppm and OH = 4×10^{-7} ppm, the rate of SO_2 oxidation is

8% per hour. Thus particle formation from the reaction of SO_2 with hydroxyl radicals will be significant under some atmospheric conditions.

The transient species HO_2 has long been postulated to play an important role in atmospheric chemistry. Davis, et al.[37] have demonstrated that HO_2 can readily react with SO_2, with the rate constant for this reaction found to be 4.4×10^2 ppm^{-1} min^{-1}. This implies that the HO_2-SO_2 reactions may be important in both tropospheric and stratospheric chemistry.

Recent modeling of reactions of SO_2 in the presence of hydrocarbons and NO_x mixtures at reactant concentration levels less than 1 ppm indicate that reactions of SO_2 with OH and HO_2 can account for up to 10% of total SO_2 reacted.[38]

$\underline{RO_x + SO_2}$

Indications are that oxidation of SO_2 by oxygenated organic radicals (RO, RO_2) may be important. Recent studies have been made of the propylene-SO_2-O_3 dark reaction to identify the specific radical responsible for the formation of SO_3. Cox, et al.[39] attributed the oxidation of SO_2 to a reactive species formed in the O_3-olefin reaction. McNelis[40] studies indicate that the reactive biradical species, RCHOO , is responsible for the oxidative consumption of SO_2. The steps of the proposed mechanism are

$$O_3 + CH_3\text{-}CH{=}CH_2 \rightarrow HCHO + CH_3\dot{C}HOO\cdot$$

$$O_3 + CH_3\text{-}CH{=}CH_2 \rightarrow CH_3CHO \underset{O}{+} H\dot{C}HOO\cdot$$

$$R\dot{C}HOO\cdot + O_2 \rightarrow \cdot OH + RCOO\cdot$$

$$\dot{R}CHOO\cdot + O_2 \rightarrow O_2 + RCHO$$

$$CH_3\dot{C}HOO \rightarrow CH_2{=}C{=}C + H_2O$$

$$\cdot OH + CH_3\text{-}CH{=}CH_2 \rightarrow CH_3\dot{C}H\text{-}CH_2OH$$

$$R\dot{C}HOO\cdot + SO_2 \rightarrow SO_3 + RCHO$$

Other Reactions

Other reactions have been postulated as possible contributors to SO_2 oxidation processes. SO_2 has been observed to react in the presence of NO_2 and O_3; it has been speculated that this could be due to reaction of SO_2 with NO_3 or N_2O_5 which are generated by the reaction of O_3 with NO_2.

Although the reaction of SO_2 with O_3 has been shown to be slow in the gas phase, there is some evidence that this reaction occurs rapidly in the presence of water droplets, and might thus be expected to occur rapidly on the surfaces of moist particles.

Oxidation Rates

Recent results from smog chamber studies at Battelle, Calspan and the University of Minnesota show that the SO_2 photooxidation rate differs from chamber to chamber by as much as two to three orders of magnitude. The highest reported rate for SO_2 in the "clean" air chamber system (6% per hour, Battelle) is comparable to that in the real, urban atmosphere and does not seem to be much affected by the presence of propylene/NO_x. Experimental study is now under way to find whether observed discrepancies in the oxidation rate reflect contaminant effects or chamber surface effects.

4.2.6.1.2 Aerosol Formation--The marked influence of SO_2 on aerosol formation in photochemical smog simulation studies is well documented. Although the exact mechanism by which SO_2 is converted into aerosol remains uncertain, these general conclusions can be drawn: (1) In the absence of SO_2, saturated hydrocarbons produce little, if any, aerosol. In the absence of SO_2, aromatic hydrocarbons and olefinic hydrocarbons with five or more carbon atoms form aerosols; those with four carbons or less do not. Dienes, terpenes and cyclo-olefins also form aerosols in the absence of SO_2. (2) SO_2 increases light scattering in studies of individual hydrocarbons and is particularly noticeable with olefins, where the increase is enormous. Increase with paraffins is moderate, and with aromatics, small. (3) SO_2 increases the condensation nuclei count in studies of hydrocarbon-NO_x mixtures. In the case of 1-dodecene and 1,3-hexadiene, only a few ppb of SO_2 are required to produce an order of magnitude effect. With aromatics only small increases are seen. (4) In general the formation of aerosol in hydrocarbon-NO_x-SO_2 systems does not occur to any appreciable extent until most of the NO is converted to NO_2 and O_3 begins to form. (5) Experimental evidence shows that SO_2 influences the reaction rate parameters in simulated smog, the degree of influence depending on such factors as realtive humidity, initial NO_2/NO_x ratio, hydrocarbon/NO_x ratio and hydrocarbon type. (6) There is controversy about the chemical composition of aerosol formed from the hydrocarbon-NO_x-SO_2 photochemical system. However, there is compelling evidence that the aerosol formed from $C<5$ olefins-NO_2-SO_2 is predominantly inorganic--mainly H_2SO_4--whereas the higher olefinic hydrocarbons produce carbonaceous aerosol as well. Studies on the propylene-P_3-SO_2 system indicate that the dominant conversion for SO_2 results in formation of H_2SO_4. In the presence of NH_3, NH_4SO_4 aerosol is observed. Infrared spectra of dried, CH_2Cl_2 extracts, of atmospheric and smog chamber aerosols, show C-H absorptions around 3 μ, C = O absorptions around

6.5 μ, C = C and/or N = O absorptions around 6.7 μ and a number of peaks at longer wavelengths. Gas chromatographic-mass-spectrometric studies indicated organic acids and nitrate esters were also present. Infrared spectra of aerosols formed from 1-heptene-NO_x with and without SO_2 indicated that with SO_2 the aerosol contained a sulfonic acid.

4.2.6.1.3 Catalytic Oxidation--Reaction rates for the system SO_2-H_2O-solid surfaces have been made. It was found that fractional collisions of SO_2 leading to reaction with Al_2O_3 and MnO_2 is $3x10^{-4}$, and with fly ash and charcoal, $5x10^{-5}$. These values suggest lifetimes of about one hour in urban plumes and 10 hours in coal-fired power plant plumes for relative humidities of 50%. Lifetimes increased as realtive humidity decreased. However, other studies of SO_2-H_2O-Fe_2O_3 indicate that reaction does not depend on relative humidity. For high SO_2 concentrations (>700 ppm) and large liquid droplets, Matteson and Giardina[41] measured a 60% increase in the mass transfer of SO_2 to the droplet if a surface charge density of 6 stat C/cm^2 was applied. The magnitude of the effect is not known for ambient SO_2 concentrations charged raindrops.

4.2.6.1.4 Physical--The solubility in water of SO_2 at low concentrations has been measured at 25.1 C as function of pH.[42] The scheme assumed was:

$$SO_{2\ gas} + H_2O_{liq} \rightleftarrows SO_{2\ aq} + H_2O$$

$$SO_{2\ aq} + H_2O \rightleftarrows H_3O + HSO^-_3$$

The second ionization

$$HSO_3^- + H_2O \rightleftarrows H_3O^+ + SO_3^{2-}$$

was assumed to be negligible. The experimental results agree well with values extrapolated from measurements at higher SO_2 concentrations by Johnstone and Leppla.[43]

4.2.6.2 Field Studies--Atmospheric data on SO_2 and particulate sulfates are available from: 1) 24-hour integrated network measurements of SO_2 and suspended water-soluble sulfates at urban and nonurban continental and maritime sampling sites in the United States, and 2) from field studies of atmospheric aerosols and gaseous smog components. Interpretation of data has emphasized: (1) the distribution of SO_2 and sulfate, (2) the relationship between SO_2 and sulfate, and (3) chemical forms of sulfur in particulate matter.

4.2.6.2.1 Distribution of SO_2--Recent analysis of national and regional trends in sulfur dioxide show a pronounced decline in sulfur dioxide levels throughout the nation.[44] Figure 4.11 shows that this downward trend for 1970-1973 occurs throughout the nation with perhaps a degree of leveling off at stations where concentrations are well below the annual standard. Based on the number of observation sites (Table 4.8), these downward trends represent general patterns in urbanized population centers, but may not adequately represent SO_2 levels near nonurban point sources. Data from background sites show that background SO_2 levels remained relatively stable in the 1970-1973 period.

Table 4.8. SURVEILLANCE CATEGORIES FOR SULFUR DIOXIDE SITES[44]
(Number of Sites)

	Geographical Area					
	Northeast	South	North Central	Midwest	West	Nation
Population-oriented	65	18	62	33	21	199
Source-oriented	1	1	2	0	0	4
Background	4	2	2	2	0	10
Total	70	21	66	35	21	213

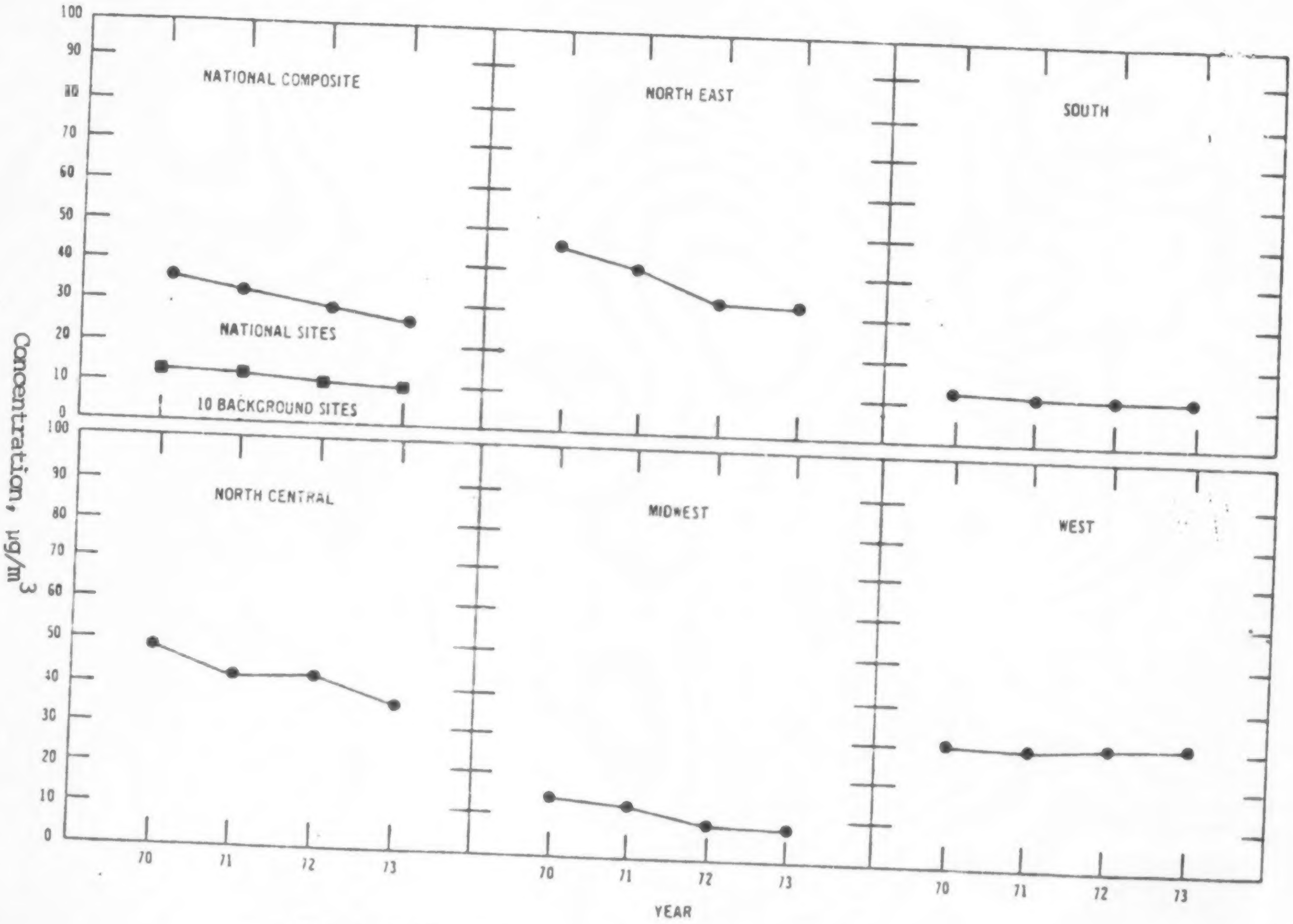

Figure 4.11. National and regional trends in sulfur dioxide, 1970-1973.

4.2.6.2.2 Relationship between SO_2 and Sulfates--Altshuller's[45] analysis of 1964-68 National Air Surveillance Networks data for SO_2 and sulfate showed that the relationship between atmospheric SO_2 and sulfate is not simple. His results showed that a reduction of SO_2 may not cause a proportional reduction in sulfate, suggesting in turn that control of other factors--hydrocarbon, NO_x, primary aerosol and NH_3--in addition to SO_2 also may be necessary to achieve acceptable low sulfate levels. A laboratory program designed to determine the effect of these factors on oxidation of SO_2 has been initiated. These effects are being studied under (1) conditions similar to those prevailing in air above an urban area, (2) conditions simulating transport where the transported pollutants receive prolonged irradiation, and (3) conditions within air masses in the vicinity of roadways.

4.2.6.2.3 Chemical Forms of Sulfur in Particulate Matter--In the past most studies have determined only the sulfate content of ambient aerosols. Craig et al.[46] have undertaken a study to establish a complete inventory of sulfur compounds present in ambient particulate matter. Seven separate chemical species of sulfur have been identified in atmospheric samples taken in California: SO_3, SO_4^{-2}, SO_2, SO_3^{-2}, S^0, and two kinds of sulfides. Sulfates were found to be the dominant species, although reduced forms of sulfur were at times comparable to the sulfate concentrations.

Novakov et al.[47] determined the chemical states of sulfur in smog particles collected in two particle size classes as a function of time of day in Pasadena, California. The sulfur content was found to be highest at night and consisted of S^{+4} species and S^{+6} species. The S^{+4}

species predominated at night on the smaller particles, and was presumed to be adsorbed SO_2 which was later oxidized to S^{+6} (SO_4^{-2}), and predominated in larger particles during the day.

In laboratory studies, Taarit et al.[48] have shown that SO_2 and MgO powder react in sunlight to form SO_3. It is likely that this reaction occurs in a liquid phase on the surface of the MgO, and may occur on all basic metal oxides in the atmosphere. The ion SO_2^- is formed by exposing V_2O_5 on silica gel and MgO to SO_2. Although SO_2 and H_2S in the gas phase react alowly, Rao and Lunsford[49] have found the reaction of the SO_2^- surface ion is rapid and yields free sulfur. They also observed the SO_4^- surface ion.

4.2.6.3 Transport and Removal--SO_2 in the atmosphere may undergo reaction with the earth's surface (grass, trees, concrete, etc.). The flux of SO_2 to ground can be expressed as

$$\text{Flux} = K_z \frac{\partial c}{\partial z}$$

where K_z = the vertical eddy diffusitivy of mass, cm^2/sec

$\frac{\partial c}{\partial z}$ = the vertical concentration gradient of SO_2 near the ground, gm/cc/cm

The flux is directly proportional to the local SO_2 concentration, and

$$\text{Flux} = vc$$

where v = proportionality constant, commonly called the "deposition velocity," cm/sec

c = SO_2 concentration

Therefore, $v = \frac{1}{c} K_z \frac{\partial c}{\partial z}$.

The three terms on the right side of the above equation can be measured. The magnitude of the deposition velocity, v, is a measure of the reactivity of the surface. The values reported recently for the deposition velocity, v, of SO_2 on a variety of surfaces are given in Table 4.9.

Table 4.9. SO_2 DEPOSITION VELOCITIES

Type of Surface	Deposition Velocity	Reference
wet leaves	1 cm/sec	50
grass	0.8 cm/sec (summer)	51
	0.3 cm/sec (autumn)	
grass	0.55 cm/sec	52
grass	0.8 cm/sec	53
vegetation (St. Louis)	.5 to 5 cm/sec	53
iron (90% relative humidity)	0.015 cm/sec	54
	0.01 cm/sec	55
zinc (90% relative humidity)	0.049 cm/sec	54
	0.063 cm/sec	55

If the deposition velocity is as large as more recent studies indicate, surface removal of SO_2 in air layers which are well mixed to the ground may dominate SO_2 removal and conversion processes.

4.2.7 Mathematical Modeling

The EPA Meteorology Laboratory concentrates most of its efforts on studies of transport and dispersion. It develops and tests mathematical models to help to relate rates of source emissions to concentrations at receptors, depending on meteorological conditions. A general discussion of modeling is given in Appendix A, Air Quality Criteria for Sulfur Oxides.[56] Models have been developed to estimate pollution concentrations over an entire city from a single large source like a power plant stack, or from a source such as a highway or an airport.

The UNAMAP (Users' Network for Applied Modeling of Air Pollution) was put into operation in May, 1973. The purpose of UNAMAP is to make available current air quality simulation models to both EPA and non-EPA users via a teletype-processing network. The models are all in the form of computer programs accessible from remote terminals connected to a central computer by telephone lines.

The six models now on UNAMAP are:

APRAC - urban carbon dioxide model.

HIWAY - hourly concentrations from roadway segments.

CDM - Climatological Dispersion Model.

PTMAX - maximum hourly concentrations from a point source.

PTDIS - hourly concentrations at various downwind distances from a point source.

PTMTP - hourly concentrations at various receptor locations from multiple point sources.

The practical application of dispersion models is shown by the following example. Studies concerned with the impact of state implementation plans on low-sulfur coal requirements predicted a probably deficit in 1975. Therefore, hourly emissions and meteorological data were used to model peak 1-hour, 24-hour and annual concentrations of SO_2 in the vicinity of 180 power plants. It was determined that 62 plants might be able to operate with full variances, 39 with limited variances and 80 with no variances. The shift in full requirements should result in an annual saving of 137 million tons of low (less than 1.0%) sulfur coal.

A different type of mathematical model[57,58] has also been developed based on actual air pollution measurements in cities at intervals of time from one hour to one year. It shows statistical relationships and is needed for interrelating air pollutant effects, air quality standards, air quality monitoring results, diffusion calculations, source-reduction calculations and emission standards.

4.2.7.1 Fluid Modeling Facility--A fluid modeling facility is being established to study the flow and diffusion of pollutants around buildings, highway configurations and complex terrain. It includes large and small wind tunnels, a model shop, electronics shop, minicomputer, photographic darkroom, classroom and offices. A contract has been awarded for the construction of a recirculated water channel/stratified towing tank. Layered mixtures of salt water will be used in the test section to produce density stratification. Dyes and shadowgraphs will be used for flow visualization.

Examples of results that can be obtained with a tow tank are found in similar work performed under EPA contract.[59] One study was of plume dispersion from an elevated source upwind of an idealized mountain under two different stability conditions. Highlights of the study were: (1) within stably stratified flow is upstream blocking that causes increased plume rise and spreading; (2) the plume tends to flow around rather than over the ridge, thus greatly enhancing the plume's lateral spread; (3) concentrations would be larger at stations on the mountain ridge than at other surface stations.

4.2.7.2 Regional Air Pollution Study (RAPS)--There is a need to develop and validate improved air quality simulation models for applying to least-cost pollution control strategies, and to other models such as those for land use, ecological and total cost effectiveness. This need was recognized in setting the objective for the Regional Air Pollution Study (RAPS), a five-year study in the St. Louis metropolitan area using an extensive base of emission, meteorological and air quality data with research on the processes of pollutant transformations, dispersion and removal. A 25-station telemetering network will provide measurements of CO, NO, NO_2, O_3, total hydrocarbons, non-methane hydrocarbons, total gaseous sulfur, SO_2 H_2S, fine particulates, total particulate and meteorological observations. Two large helicopters from EPA's Environmental Research Center at Las Vegas are outfitted to measure most of the parameters measured at the fixed stations. Considerable effort has been spent setting up data formats and developing software from the RAPS data bank, which will include emission data and models, all data from the aerometric network, meteorological upper air sounding data, and most data from special studies to be performed in conjunction with RAPS.

Studies have already been performed to describe the urban boundary layer structure with emphasis on morning and evening transition periods and investigators have made extensive measurements of aerosols in and around St. Louis. Most special studies are being done cooperatively with the METROMEX project, which is concerned with the increased precipitation amounts observed downwind from large urban or industrialized areas.

4.2.7.3 Large Power Plant Effluent Study (LAPPES)--The Large Power Plant Effluent Study (LAPPES) was to determine the pattern of ground-level concentrations of pollutants released to the atmosphere from large coal-burning mine-mouth power plants. Four volumes of basic data obtained from the LAPPES project have been published.[60-63] Early analyses indicate that tall stacks help to reduce or sometimes eliminate significant ground level concentrations under some meteorological conditions, particularly in the stack's vicinity. However, the study also showed that there are some things tall stacks cannot do. For example, reasonably increasing stack height will not significantly reduce episodic ground-level concentrations of a plume trapped within a limited mixing layer; if emissions increase, so will ground-level concentrations. Washout of SO_2 from the plume was also studied in the LAPPES. The effect of precipitation falling through the plume seems to bring SO_2 closer to the ground.

4.2.7.2 Rough Terrain Effects--According to theoretical estimates, high concentrations of air pollution can occur when a plume from a stack encounters high ground, and we need to know if such concentrations can actually occur. Field studies using tracers have been conducted in rough or mountainous area, one such having been done cooperatively with the AEC at Huntington Canyon, Utah.[64] There it was found that depending on atmospheric stability conditions, dispersion rates were 4-15 times greater than might have been estimated using customary procedures. More rough terrain field studies are planned.

4.2.7.5 Highway Studies--In the past few years more and more governmental and private groups have used highway (line source) air quality models for environmental impact statement (EIS) preparation and review. Although several mathematical models have been developed for highway evaluations, little is known about the initial spread of pollution due to the turbulent wake of vehicles and subsequent dilution within the first hundred meters of travel from the highway. The Meteorology Laboratory has sponsored a tracer study of dispersion within the immediate vicinity of a highway.[65] An inert tracer gas (sulfur hexafluoride) was dispersed from a vehicle moving in the traffic stream of a six-lane highway for sampling at 12 locations at distances of about 100 meters downwind and 20 meter upwind. Carbon monoxide was measured simultaneously. Early results indicate that vertical dispersion in the immediate vicinity of the highway is larger than assumed in the EPA HIWAY model and that the turbulent wake significantly affects concentrations.

4.2.7.6 Airport Studies--Two field studies have been conducted at airports. The first,[66] at Washington National Airport, was to validate and further develop an existing mathematical dispersion model.[67] For six months continuous records of air quality, meteorological and operational records were compiled. Carbon monoxide, particulates, nonmethane hydrocarbons and nitrogen dioxide were sampled at eight locations. The final result showed the modified model to consistently predict mean and median values for CO and particulates (ranging from 16% under prediction to 36% over prediction). These validation results were without calibration of any kind. Better results are expected in the future when the model will be calibrated. The second study,[68] at Atlanta International Airport, was to determine the effect of experimental aircraft emissions control operations on air quality. The emissions control procedure consisted primarily of shutting down one engine by approved aircraft during taxiing from landing runway to terminal building. A network of eight monitoring stations was used. While a maximum hourly reduction of about 15% occurred in aircraft emissions, the instrument network did not detect a statistically significant reduction in air quality levels which could be attributed to emission control procedures.

4.2.7.7 Precipitation Washout of Sulfur Compounds--A model for the washout of sulfur dioxide from power plant plumes has been developed[69,70] based on reversible gas absorption phenomena. It can be used for predicting washout of pollutant gases other than sulfur dioxide, with substitution of appropriate physical properties. The model is based on concepts of reversible behavior and negligible plume distortion by the washout. Field experiments showed that sulfur dioxide concentrations in rain can be calculated within a factor of two of observed values, although predictability is reduced in the immediate vicinity of the source and complicated by the occurrence of chemical reactions.

Conclusions from the model, verified by observation, are:

1. Washout of sulfur dioxide from a concentrated, high-elevation plume can be obscured by the presence of low-elevation, low-concentration background levels;

2. The acidity of rain strongly influences its sulfur dioxide scavenging potential and

3. Negative washout occurs as the result of desorption of sulfur dioxide from the rain below the sulfur dioxide plume.

Sulfate washout measurements were also made. Results indicate that the rate of sulfur removal via sulfate washout is up to five times more rapid than that via sulfur dioxide washout.

5.2.7.8 Precipitation Scavenging of Inorganic Pollutants from Metropolitan Source--In the summers of 1972 and 1973 field experiments were conducted in the St. Louis area to measure the precipitation scavenging of inorganic pollutants.[71] Concentration measurements of collected rainwater have shown that precipitation scavenging by convective storms can be an effective mechanism for removal of urban pollutants from the atmosphere. Results of the study indicate that scavenging removal rates can be comparable to urban emission rate estimates.

4.2.7.9 Simulation of the Photochemical Reaction Processes Within a Power Plant Plume--Based on studies of chemical mechanisms observed in smog chambers a preliminary plume dispersion model has been developed to investigate $SO_2 \rightarrow SO_4^=$ transformation in power plant plumes. Preliminary results indicate transformation rates of 2-3% per hour. Higher rates of about 20% per hour were reported by TVA investigators.[72] Results from another study[73] agree with the model. Large concentrations of particulate in the TVA plume may have caused more rapid SO_2 conversion because of catalytic reactions. In the other study the plumes had low particulate concentrations and therefore only homogeneous gas phase conversion processes were important.

4.2.7.10 High Surface Ozone Concentrations--Recently, high surface ozone concentrations have been observed in rural areas remote from urban centers, with values at times exceeding the National Ambient Air Quality Standard. Consequently, mechanisms for bringing ozone down from the stratosphere, formation during lightning discharges, and near surface chemical processes were reviewed. High surface values can be caused by direct transport downward from the stratosphere through the jet stream region behind strong cold fronts and by convective activity transporting downward ozone previously injected into the upper troposphere. Lightning contributes only brief small rises in ozone concentration, a conclusion agreeing with observations of thunderstorm effects made in a study of ozone conditions near 33 cities during summer, 1971.[74] Chemical reactions make significant contributions over a period of time, but chemical and physical processes that cause high surface ozone concentrations are not well understood. Laboratory and field studies are in progress. In one instance computerized meteorological data from regularly reporting stations, compiled on a global scale, is being used to prepare trajectories automatically for tracing the origin of air in which high ozone concentrations have been observed.

4.2.7.11 Los Angeles Reactive Pollution Project (LARPP)--During the Los Angeles Reactive Pollution Project (LARPP), a photochemical field experiment, parcels of air were followed by especially instrumented helicopters and mobile van in order to determine changes in reactive pollutants. The helicopters were tracked by radar and guided by balloons that floated at near constant levels. Tracer materials were also released and sampled. Results of this project are to be reported in the Santa Barbara, California, workshop-symposium to be conducted November 12-14.

In connection with LARPP a team from the Meteorology Laboratory made special solar radiation observations from August 30 through

November, 1973. Six stations were instrumented, one of which was on a mountain at 6000 feet elevation. As expected, atmospheric pollution substantially reduced incident ultraviolet energy. For example, when visibility at El Monte was approximately three to five miles (a common occurrence during the pollution season), the incident ultraviolet energy was typically about 30 to 40% less than that received on top of the mountain, depending on solar elevation. In the absence of pollution the difference would have been expected only to be about 5% less. Obviously, the top of a pollution layer receives considerably more ultraviolet irradiance than the bottom layer. Most photochemical models today treat ultraviolet energy in a simplistic way and do not account for its vertical variation through the pollution layer. It has been suggested that these models improved by allowing for such vertical variation of the ultraviolet radiation.

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5. EFFECTS

5.1 HEALTH

5.1.1 General Discussion

The Clean Air Act amendments of 1970 mandated that the Administrator of the U.S. Environmental Protection Agency promulgate ambient air quality standards for substances that may be emitted into the atmosphere and thereby represent potential health hazards.

To fulfill the mandate, standards were established which in compliance with the law were designed on the basis of the best information available to include a margin of safety sufficient to assure protection of the most sensitive segments of our population. Because the information base on which standards were established was incomplete, the agency committed itself to a continuing research program designed to determine their adequacy.

As results from this and other research efforts around the world become available, it is necessary to reappraise and update the health basis for the standards, as is done in this document.

5.1.2 Nitrogen Oxides

5.1.2.1 Human Studies--The National primary standard for nitrogen dioxide is 100 $\mu g/m^3$ (0.05 ppm) annual arithmetic mean.

5.1.2.1.1 Evidence upon which standard was based--The existing primary NO_2 standard of 100 $\mu g/m^3$ was based primarily on the Chattanooga School Children studies[1,2,3] conducted from November, 1968 through April, 1969. Long-term exposure to ambient NO_2 concentrations between 117 and 205 $\mu g/m^3$ (0.062 and 0.109 ppm) accompanied by suspended nitrate concentrations between 4 and 6 $\mu g/m^3$ for six months and longer was associated with the following effects: (1) an 18.8% excess in acute respiratory illness in families; (2) significantly decreased lung function ($FEV_{0.75}$) in elementary school females; and (3) significantly increased bronchitis morbidity in elementary school children exposed for two and three years.

5.1.2.1.2 Interim evidence (1969 through January 1, 1973)--Estimates of community exposure to NO_2 in the initial Chattanooga study were derived from air monitoring data obtained with gas bubblers employing the 24-hour Jacobs Hochheiser method. Since the time of the study, the Jacobs Hochheiser method has been found unreliable, creating the need to reevaluate the relationship between quantitative exposure level and observed adverse health effects in Chattanooga using data obtained with other methods of monitoring.

Alternate exposure estimates were derived from the network air monitoring stations established by the Division of Abatement, National Air Pollution Control Administration (U.S. Public Health Service) in the Chattanooga, Tennessee - Rossville, Georgia interstate area. Continuous recordings of NO_2 were taken, utilizing the colorimetric Saltzman technique at ten stations from December, 1967, through November, 1968. A complete report of data obtained from this network is given in the publication Chattanooga, Tennessee - Rossville, Georgia Interstate Air Quality Study 1967-1968 (U.S. Department of Health, Education and Welfare, National Air Pollution Control Administration Publication No. APTD-0583, 1970).[4]

Observed NO_2 concentrations, wind speed and direction and topographical characteristics were used to obtain NO_2 exposure. Although health data were collected from November, 1968, through April, 1969, in the initial Chattanooga study (the six months immediately after the period of monitoring by the Division of Abatement), NO_2 exposures of the affected communities probably did not change substantially from those measured from December, 1967, through November, 1968, because TNT production by the Volunteer Army Ammunition Plant remained at peak capacity throughout these months of 1968 and 1969.

In the original Chattanooga health studies, the frequency of sampling for NO_2 exposures using the now discredited Federal Reference Method allowed dissociations of adverse health effects only with daily or annual average NO_2 concentrations. Air monitoring data from the national abatement air monitoring network using the continuous Saltzman NO_2 method provided additional information on hourly and daily frequency distributions of NO_2 concentrations. Experimental animal studies suggested that short-term peak exposures lasting for two to three hours were sufficient to account for excesses in acute respiratory diseases. Therefore, the 90th percentile of the frequency distribution observed for hourly concentrations measured by the Saltzman method was selected as a more appropriate estimate of NO_2 exposure for relating to the observed adverse health effect in the original Chattanooga study. Ideally one would like to look at maximum hourly distributions as well. An excess of acute respiratory illness among families was observed consistently when the 90th percentile of hourly NO_2 concentrations was 376 $\mu g/m^3$ (.20 ppm) or above. When similar hour exposures were 188 to 282 $\mu g/m^3$ (0.10 to 0.15 ppm), the evidence was not consistent. In the study on bronchitis rates in children, a measure of more severe respiratory disease, children exposed for two or three years to peak hourly NO_2 concentrations of 188 to 282 $\mu g/m^3$ (0.10 to 0.15 ppm) had significantly higher bronchitis rates than children in the lowest exposure neighborhood.[5]

5.1.2.1.3 New Evidence (Since January, 1973) Recent Nitrogen Dioxide Exposure in Chattanooga, Tennessee--Since the initial CHESS study in Chattanooga, Tennessee, a vigorous pollution control program by the Department of Defense and a decrease in TNT production has been accompanied by a decrease in NO_2 emissions, evidenced by a decrease in the mean of the annual average levels of NO_2 in the most exposed study neighborhoods from 282 $\mu g/m^3$ in 1968 to 56 $\mu g/m^3$ in 1973. (Table 5.1) Despite these lower annual NO_2 levels, the population living in the community in 1972 with the highest annual average exposure to NO_2 continued to experience repeated short-term exposure to NO_2 as measured by the 90th percentile of average daily concentrations (75 to 220 $\mu g/m^3$). (Table 5.2) The 90th percentile of the maximum hourly NO_2 values ranged from 228 to 815 $\mu g/m^3$ in 1972 (Table 5.3). In 1968 and in 1971, the neighborhoods closest to the plant also were exposed to relatively high levels of suspended nitrates (5.0-6.0 $\mu g/m^3$). In the intermediate exposure community, the mean of the annual average NO_2 levels also fell (113 $\mu g/m^3$ in 1968 to 49 $\mu g/m^3$ in 1973 - Table 5.1). Short-term exposures in this community were decreased from former high levels, but still the 90th percentile of the maximum hourly values of about 116 to 164 $\mu g/m^3$ were noted on 36 days each year (Table 5.3). In the low exposure area, the mean of the annual average NO_2 exposures were also reduced from 56 down

Table 5.1. ESTIMATED AVERAGE ANNUAL POLLUTANT EXPOSURE LEVELS IN THREE STUDY AREAS IN CHATTANOOGA, TENNESSEE, 1968-1972[4]

Pollutant	Sector and Exposure Ranking*	Average Annual Concentration, $\mu g/m^3$ (Arithmetic Mean)				National Air Quality Primary Standard Annual Average
		1968	1970	1971	1972	
Nitrogen Dioxide	I-Low	56*	45**	45**	43***	100 $\mu g/m^4$
	II-Intermediate	113*	45**	45	49***	
	III-High	150-282*	43	52*	56***	
Suspended Nitrates	I-Low	2	1	2	NA	None
	II-Intermediate	3	2	3	NA	
	III-High	6	3	6	NA	
Suspended Sulfates	I-Low	12	13	10	NA	None
	II-Intermediate	10	13	10	NA	
	III-High	10	13	10	NA	
Total Suspended**** Particulates	I-Low	62	64	64	68	75 $\mu g/m^3$
	II-Intermediate	72	63	62	62	
	III-High	81	51	52	51	

*NO_2 Date - Saltzman Colorimetric

**Estimated from trend observed in high exposure area.

***NO_2 Data - chemiluminescence

****Geometric mean

Table 5.2 DAILY NITROGEN DIOXIDE CONCENTRATIONS OBSERVED AT CHATTANOOGA AIR MONITORING STATIONS[4]

Community Exposure	NAPCA Abatement Station Number	Station Number	Daily NO_2 Values				
			Year	Annual Average	90th Percentile	99th Percentile	Maximum
High	19	31	1968	395	921	1466	1880
			1972**	91	220	333	359
			1973	60	118	185	268
	15	32	1968	150	282	526	827
			1970	41	68	120	123
			1971	57	91	147	155
			1972**	46	75	104	136
			1973	44	64	106	164
	17	33	1968	188	489	959	1203
			1970	55	95	200	236
			1971	54	94	150	163
			1972**	49	76	107	114
			1973	39	63	122	176
	20	34	1968	282	677	1166	1711
			1972**	37	76	136	178
			1973	31	55	77	90
Intermediate	161	21	1968	150	320	714	752
			1972**	41	64	82	91
			1973	41	62	86	91
		22	1968	-	-	-	-
			1972**	56	78	111	142
			1973	63	89	112	122

Table 5.2. (continued)

	41	1968	-	-	-	-
		1972**	43	62	75	76
		1973	57	84	110	120

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*1968, 1970 and 1971 concentrations measured by Saltzman method. 1972 and 1973 concentrations measured by chemiluminescence method.

**Only last four months of 1972 monitored.

to 43 $\mu g/m^3$ (Table 5.1). Peak hourly exposures on all but a few days were much like those of the intermediate exposure community.

This set of circumstances provided the opportunity to assess whether or not individuals experiencing a decrease in annual average exposure to NO_2 levels, but still exposed to intermittent high levels of NO_2, would continue to experience significant adverse health effects.

Prevalence of Chronic Respiratory Symptoms in Chattanooga 1971[6]

The frequency of chronic respiratory disease symptoms was increased during or right after the previously mentioned high exposure period (1968-1970) only in the most heavily impacted area where increases in symptom frequency, which are not statistically significant, were observed three years after the high annual NO_2 exposures were reduced 43 to 56 $\mu g/m^3$. However, peak short-term NO_2 exposures continued. This increase in symptoms might represent a residual effect from previous excessive long-term exposures or it might indicate that prior high exposures coupled with peak current exposures are sufficient to trigger the onset of chronic respiratory disease symptoms. The presence of elevated levels of suspended nitrates may also be a contributing factor.

Lower Respiratory Disease and Nitrogen Dioxide Retrospective Survey in Chattanooga, Tennessee, 1971[7]

Acute lower respiratory disease morbidity in the period 1969-71 was surveyed retrospectively among children one to 12 years of age from the three original CHESS communities representing an exposure gradient for NO_2 (Table 5.4). Lower respiratory disease morbidity rates among children of residential families residing in areas exposed to high and intermediate levels of nitrogen dioxide continued to be significantly higher

Table 5.3. MAXIMUM HOURLY NO_2 CONCENTRATIONS BY COMMUNITY AND STATION
CHATTANOOGA, TENNESSEE, 1970-73*[4]
(Micrograms per Cubic Meter)

Community Exposure	Abatement Station Number	CHESS Station Number	Year	Annual Arithmetic Average	Nitrogen Dioxide ($\mu g/m^3$) 90th Percentile	99th Percentile	Maximum
High	19	31	°72	346	815	905	906
			°73	230	522	864	977
	15	32	Δ70	106	225	488	564
			Δ71	152	270	526	940
			°72	116	228	530	669
			°73	103	157	398	752
	17	33	Δ70	222	450	1090	1109
			Δ71	165	350	690	1128
			°72	164	304	549	599
			°73	127	235	655	752
	20	34	°72	123	272	485	627
			°73	87	169	257	376
Intermed-	161	21	°72	77	116	150	154
			°73	87	124	188	700
		22	°72	105	143	265	270
			°73	113	164	248	338
Low		41	°72	85	113	159	187
			°73	105	150	183	216

°CHESS Chemiluminescent

ΔCHESS Saltzman

Table 5.4. THREE-YEAR FREQUENCY OF "ANY LOWER RESPIRATORY DISEASE" AND BRONCHITIS: MODEL PREDICTED RATES FOR CHILDREN AGED ONE TO 12 YEARS FROM HOUSEHOLDS WITH A HIGH SCHOOL EDUCATION OR GREATER[7]
(1969-1971)

Morbidity Condition	Number of Episodes		Model Predicted* Rates, %			High/Low Community ($p < 0.01$)
			I-Low	II-Intermediate+	III-High	
"Any Lower Respiratory Disease"	One or More	Male	28.3	28.9	38.5	1.36
		Female	28.0	30.9	36.5	1.30
	Two or More		14.0	17.0	20.2	1.44
Bronchitis	One or More	Male	12.2	13.9	19.8	1.62
		Female	9.8	16.1	20.0	2.04
	Two or More	Male	4.4	8.8	10.5	2.39
		Female	4.2	9.8	9.6	2.29

*Age, education head of household adjusted rates for nonasthmatic children with three or more years residence duration.

+Intermediate exposure community significantly higher than low exposure community in 5/8 sex by number of episode categories but significantly lower than high exposure community in only 2/8 categories.

than those of comparable children living in a low exposure area. Furthermore, lower respiratory illness rates in intermediate exposure neighborhoods were significantly lower than rates in the high exposure community.

Because this study was not designed to determine yearly rates, it was not possible to assess whether the significantly higher rates in the intermediate- and high-exposure communities were consistent over the three study years or were heavily weighted by the single year, 1969, when annual mean NO_2 levels were above the primary standard.

Incidence of Acute Respiratory Disease, Chattanooga, Tennessee, 1972-1973[8]

A study of acute respiratory disease was conducted in 1972 and 1973 in the three Chattanooga CHESS communities. In the 1972 study the excess risk of acute respiratory disease remained consistently higher for those living in the high-pollution community compared to those in the low-pollution community. (Table 5.5) As was noted in an earlier study, the highest excess risk (50%) was observed in pre-school children. The intermediate exposure community also showed excess risk of lower respiratory disease compared to the low-pollution community. Moreover, excess risk for total respiratory disease was not as great in the intermediate community as in the high-pollution community. Pre-school children living in the intermediate exposure area had a lower excess risk than other age groups in that community. In the second year of study, the pattern persisted across the three communities, but the excess risks themselves were lower than the preceding year.

The excess risks of acute respiratory disease in the 1972 study were similar to those found in the earlier 1968-69 Chattanooga study. Although the annual average NO_2 levels in the initial study were substantially higher than those in the 1972 study, short-term 90th percentile hourly NO_2 exposures associated with an effect were similar in the two studies ($\sim$300 $\mu g/m^3$ in the high-exposure area in the 1972 study).

Table 5.5. RELATIVE RISK FOR TWO STUDY PERIODS OF ACUTE RESPIRATORY ILLNESS FOR STABLE FAMILIES LIVING IN COMMUNITIES EXPOSED TO DIFFERING LEVELS OF AIR POLLUTION[a,8]

Family Segment	Sector	Acute Respiratory Illness[b]				All Respiratory Illnesses	
		Involving Upper Tract		Involving Lower Tract			
		Study I	Study II	Study I	Study II	Study I	Study II
Mothers	1	1.00 (4.53)	1.00 (2.15)	1.00 (1.65)	1.00 (2.17)	1.00 (6.24)	1.00 (4.41)
	2	1.24	1.00	1.16	1.17	1.21	1.10
	3	1.28	1.20	1.68	1.05	1.40	1.12
Fathers	1	1.00 (3.06)	1.00 (1.52)	1.00 (1.20)	1.00 (1.75)	1.00 (4.30)	1.00 (3.35)
	2	1.08	.81	1.48	.95	1.19	.89
	3	1.28	1.18	1.55	.92	1.36	1.04
School Children	1	1.00 (5.06)	1.00 (2.50)	1.00 (1.84)	1.00 (2.84)	1.00 (7.05)	1.00 (5.44)
	2	1.19	1.06	1.58	1.10	1.28	1.08
	3	1.31	1.14	1.48	1.31	1.34	1.22
Pre-School Children	1	1.00 (7.00)	1.00 (3.69)	1.00 (3.56)	1.00 (5.01)	1.00 (10.69)	1.00 (8.81)
	2	1.03	.79	1.12	.92	1.07	.87
	3	1.51	1.01	1.55	1.35	1.51	1.21

[a] Study Period I--January 23, 1972 to May 21, 1972.

[b] Study Period II--September 10, 1972 to April 28, 1973.

(Table 5.6) At this time it is not know to what extent those families living in the neighborhood experiencing the highest short-term exposures of NO_2 as well as elevated levels of suspended nitrates contributed to excess risk in the total high-exposure community.

That persistence of excess risk for acute respiratory disease four years after long-term exposure has decreased may reflect residual effects from previous prolonged exposure, the effects of intermittent high peak exposures or both these factors. Findings for pre-school children in the 1972-73 study suggest the latter may be the case. The pre-school children in the high-pollution community had limited prolonged exposure to high annual average levels of NO_2 but did have short-term high exposure, yet these children showed the highest excess risks in their community. Their counterparts in the intermediate community had the lowest risk. However, excess risk persisted in the other age groups living in the intermediate exposure community, suggesting a residual effect from previous annual average exposure to NO_2 of 150 $\mu g/m^3$, (Table 5.6) or 90th percentile hourly exposure of ∿300 $\mu g/m^4$.

Ventilatory Function in School Children in Chattanooga, Tennessee 1971

Studies showed ventilatory function of children in Chattanooga was no longer impaired two years after annual exposures were reduced from ∿150-282 $\mu g/m^3$ to 43 $\mu g/m^3$ even though short-term peak hourly exposures continued to range from 228 to 815 $\mu g/m^3$ for 10% of the days each year.

Asthma Panel Studies[9]

In recent unpublished studies the EPA CHESS program in the New York-New Jersey metropolitan area, increased asthmatic attacks were

Table 5.6. HOURLY NITROGEN DIOXIDE CONCENTRATIONS OBSERVED AT CHATTANOOGA AIR MONITORING STATIONS*[8]

Community Exposure	NAPCA Abatement Station Number	CHESS Station Number	Hourly Values				
			Year	Annual Average	90th Percentile	99th Percentile	Maximum
High	19	31	1968	395	1203	3290	7144
			1972**	91	256	682	906
			1973	60	133	429	997
	15	32	1968	150	301	1128	3384
			1970	40	94	198	564
			1971	55	113	226	940
			1972**	46	84	193	669
			1973	44	85	150	752
	17	33	1968	170	496	2068	4606
			1970	54	122	414	1109
			1971	52	113	326	1128
			1972**	49	94	273	599
			1973	39	73	235	752
	20	34	1968	263	865	2670	7144
			1972**	36	81	270	627
			1973	31	66	150	376
Intermediate	161	21	1968	150	320	1448	2914
			1972**	42	73	115	154
			1973	41	75	122	700
	-	22	1968	-	-	-	-
			1972**	56	94	160	270
			1973	63	110	160	338

Table 5.6. (continued)

Low	-	41	1968	-	-	-	-
			1972**	43	74	113	188
			1973	56	99	142	216

*1968, 1970 and 1971 concentrations measured by Saltzman method. 1972 and 1973 concentrations measured by chemiluminescence method.

**Only last four months of 1972 monitored.

significantly associated with elevated levels of suspended nitrates when temperatures were 50°F or above.[10] No such effect was observed with NO_2. Chemiluminescence instruments showed NO_2 levels met the annual average standard at a central city station but only the old (now discarded) Federal Reference Method was used for measurement of NO_2 in study neighborhoods themselves.

In another study conducted by the same group in to Southeast communities, there was evidence of excess risk of asthmatic attacks associated with elevated levels of suspended nitrates, but the findings were less consistent than those observed in the New York study.[11] Because of problems in present methods to measure and analyze suspended nitrates, findings in these studies should be viewed qualitatively rather than quantitatively. These two studies raise a question as to levels of NO_2 which might be necessary to prevent levels of transformation products, such as nitrates, which in themselves may contribute to adverse health effects.

Preliminary analyses of California asthma panel studies show no easily demonstrable increase in attack rates occurs with NO_2 exposures ranging up to 400 $\mu g/m^3$ for one hour and 200 $\mu g/m^3$ for 24 hours. However, effects of other stronger illness determinants, like aerosols containing sulfates and nitrates, had not been disentangled at the time of the present summary.

Indoor No_2 Studies

Preliminary measurements by EPA of NO_2 indoor air concentrations show peak hourly levels in the range of 470-940 $\mu g/m^3$ (0.25 - 0.50 ppm) in the heating zone of persons cooking with gas stoves. The highest peak indoor NO_2 concentrations measured was about 1 ppm. EPA's CHESS studies suggest a greater relative risk of acute lower respiratory illness among occupants of homes with gas stoves. Mothers were the only family segment significantly affected. Presumably this excess could be related to periodic hourly NO_2 exposures in the 0.25-1.0 ppm range. Followup studies in CHESS, however, have not confirmed a relationship between air pollution due to gas stoves or gas space heaters and lower respiratory disease in mothers. A study in Ohio also did not find any respiratory disease health effect related to gas cooking. In all three health studies, measurements of indoor NO_2 air pollution were not related directly to health. Like EPA, those investigators also found increased peak indoor NO_2 levels, generally about 470 $\mu g/m^3$ (0.5 ppm) but at times as high as 940 $\mu g/m^3$ (1.0 ppm), to be associated with gas cooking. Thus, there are still questions as to whether or not indoor hourly NO_2 air pollution in the range of 0.25-1.0 ppm is related to increased risk of respiratory disease. Such a relationship would be qualitatively consistent with data in experimental animals showing an effect of short-term NO_2 exposure on resistance to infection.

5.1.2.1.4 Other new evidence--Von Nieding and associates[12] studied the acute effects of experimental NO_2 exposures on healthy and diseased subjects using pulmonary ventilation, diffusion and perfusion as endpoints. Exposure of 16 healthy subjects to 9400 $\mu g/m^3$ (5 ppm) No_2 for 15 minutes caused a significant decrease in diffusing capacity. Fourteen subjects with chronic respiratory disease showed a significant decrease in arterial partial pressure of oxygen and a significant increase in the alveolar-arterial oxygen pressure gradient upon exposure to 7520 or 9400 μg/m^3 for 60 minutes while no effect was observed at NO_2 concentrations of 3760 μg/m^3 (2 ppm). Healthy subjects (n=39) and those with chronic respiratory disease (n=70) were exposed to 30 breaths of NO_2 at concentrations over a range of 1880 to 9400 μg/m^3 (1 to 5 ppm). These subjects demonstrated increased airway resistance at NO_2 concentrations of 3000 to 3800 μg/m^3 (1.6 to 2.0 ppm). At lower concentrations, NO_2 exerted no effect, but airway resistance markedly increased as concentrations exceeded 3800 μg/m^3 (1.6 to 2.0 ppm).

Kennedy[13] studied a group of 100 coal miners with a history of exposure to nitrous fumes from shotfiring in the mine. Eighty-four of the mean had emphysema based on a residual volume of more than 150%. The 16 miners with a residual volume less than 150% of normal had less exposure to fumes than the remaining 84 men. Kennedy compared the pulmonary function of the miners exposed to nitrous fumes with non-exposed miners and those with simple pneumooconesis and found the indirect maximum breathing capacity, vital capacity, total lung capacity and residual volumes showed a markedly higher percentage of abnormal values in the nitrous-exposed group. The primary and secondary charges of the hydrox shells used in the mines were largely nitrates and fume analysis revealed (NO and NO_2) up to 88 ppm after normal firing and up to 167 ppm after misfires.

A full report of the study of chronic bronchitis among housewives aged 30 or more living in six localities throughout Japan conducted during the winter of 1970-71 is not yet available in the U.S., but a summary of this study has been made available.[14] This is the study on which the

Japanese standard of 0.02 ppm 24-hour annual average is based. The prevalence rate of chronic bronchitis was found to exceed 5% only in those areas where the annual NO_2 concentration was 0.042 ppm (79 μg/m^3) or above. However, total suspended particulate concentrations were also very high, ranging from twice to six times the U.S. primary standard indicating that the pollutant-disease association in the study cannot be ascribed to NO_2 alone.

In a study by Speizer et al.,[15,16,17] the prevalence of chronic nonspecific respiratory disease was assessed using a modified version of the Medical Research Council's respiratory disease questionnaire in a population of 268 policemen exposed to a spectrum of levels of automobile exhaust as traffic officers, patrol car officers and indoor clerical officers. The over-all prevalence of disease in the policeman population was 36.9%, and two-thirds of chronic conditions were chronic bronchitis. There was a clear relationship between smokers and the prevalence of disease. In nonsmokers and current smokers, men with greater duration of exposure in traffic tended to have higher disease prevalence rates, but the difference was not statistically significant. Measurement for exposure to automobile exhaust was limited, since only 16 work stations out of a total of 58 were chosen for study, and sampling at each station was conducted for only two days during each season of the year. The NO_2 values ranged from a minimum of 0. 005 ppm to 0.090 ppm while carbon monoxide ranged from 1 ppm to 44 ppm and hydrocarbons from 4.4 to 15.8 ppm.

In a recent preliminary report, Sprey[18] correlated death rates from hypertensive and arteriosclerotic heart disease and lung cancer with annual NO_2 concentrations. The author's data source was the National Air Surveillance Network which operated a single station in each of 42 metropolitan areas. NO_2 was measured once each two weeks by the Jacobs Hochheiser method. The twenty-six values for the year 1962 were averaged and were correlated with cause-specific death rates for the years 1959-1961.

The results showed a linear relationship with annual NO_2 concentrations for 1962. Higher death rates were found even in areas with NO_2 concentrations below the primary national standard, when compared with the lowest NO_2 areas (56 $\mu g/m^3$, .03 ppm). Adjustments for area differences in family income and education, population density, temperature and sulfate and nitrate concentrations did not affect the basic association between NO_2 and death rates. A similar linear relationship was shown for lung cancer deaths among males and females over 65 years and NO_2 concentrations in the 42 areas. The relationship was not weakened by adjustments for area differences in SO_2, sulfates, nitrates, climate, socioeconomic factors and population density.

The quantitative basis of NO_2 exposures in Sprey's work is open to question because of the limited number of air monitoring stations used as well as the unreliability of the measurement technique. However, the qualitative nature of the work should draw attention to possible extra pulmonary systemic effects of ambient NO_2.

5.1.2.1.5 General discussion of NO_2 Human Studies--Studies of NO_2 and human health effects are limited, and many conducted thus far are confounded by the presence of high levels of other pollutants. In addition, measurement data used in these studies were limited either by use of too few sampling stations or the use of an unreliable method for measurement of NO_2 or both of these factors.

Five categories of human health effects have been identified in association with NO_2: acute toxic, often fatal, reactions, diminished lung function, structural and bronchial changes of lung most likely to promote development of chronic respiratory disease, susceptibility to infection and systemic effects.

There is sufficient information from both human and animal studies to determine the levels of NO_2 which may contribute to toxic, often fatal, reactions. There is some evidence to show that prolonged exposure to NO_2 levels of 117 $\mu g/m^3$-205 $\mu g/m^3$ can contribute to increased prevalence of chronic bronchitis, increased incidence of acute lower respiratory disease and diminished pulmonary function in school children. Unanswered questions still remain with respect to short-term exposure of NO_2 and the effect on acute and chronic disease, those levels of NO_2 which may contribute to systemic effects and levels of NO_2 which may be necessary to control possible adverse health effects from suspended nitrates.

5.1.2.2 Animal Studies

5.1.2.2.1 Biological effects of NO_2--The toxicological aspects of NO_2 have been reviewed recently in these documents to which EPA has had direct input and liaison: (1) NATO Committee on the Challenges of Modern Society, "Air Pollution: Air Quality Criteria for Nitrogen Oxides," (N. 15) June, 1973;[19] and (2) The National Academy of Sciences, "Air Quality and Automobile Emission Control," No. 93-24, September, 1974.[20] Material contained here treats only a few reports in the literature which are considered significant and which have been published since these reviews were compiled, and material which is now being prepared by various known sources. NO_2 biological work being carried out currently in EPA is discussed in some detail. The possible relevance of such information is discussed in the light of previous data and predicted future possiblities.

5.1.2.2.1.1 Pathological effects of NO_2 on the respiratory track--Action of NO_2 on the respiratory tract has been reviewed previously. Its proclivity to elicit necrobiosis and desquamation of Type I alveolar epithelial cells with subsequent replacement by Type II cells and eventual regression to normal is well-known. Such changes are not specific for NO_2, but occur with O_3 and hyperbaric oxygen,[21,22] and are probably indicative of lung reaction to an oxidant or possibly any irritant at this level. Changes are induced by approximately 2 ppm NO_2 and above. Exposure to higher concentrations, 10-25 ppm on a continuous basis for 3-12 months has induced pulmonary emphysema-like disease in rats, mice, dogs and rabbits.[23-35] Lesions have been studied in detail, principally in the rat for a number of years. In the rat the disease does appear to be emphysema, since the lungs are enlarged and contain fewer air spaces, presumably from rupture of alveolar septae. Four recent studies have examined the lesion phenomenon to determine (a) if it is a problem associated with pulmonary growth, (b) whether it mimics natural disease, (c) what is the physical mechanism of its production and (d) whether interaction with ozone enhances its induction or severity.

Two studies have examined developmental features of the disease in rats by means of morphometry and post mortem pressure-volume studies. One, primarily on oxidant (ozone), showed that while exposure to 0.2 ppm oxidant resulted in significant increase in lung volume and loss of lung elasticity (lung recoil), no such effects were noted at 0.2 ppm in NO_2.[36] (Table 5.7)

The other study designed presumably to answer the question of lung maturation showed that while exposure to 15 ppm NO_2 from before birth to 65 days of age resulted in slowing of lung growth (interpreted as being due to slowed general growth for the first 10 days), the animals subsequently caught up and had essentially normal alveolar maturation at 65 days.[35] (Table 5.8)

One of these studies[36] examined the physical mechanism of lung enlargement associated with both NO_2 and ozone exposure. The data indicate that exposure to 0.2 ppm ozone produced a stretching of the stroma and loss of lung recoil.[36] The implications of this change may be rather important in exposure to oxidant, NO_2 and possibly other factors such as exposure to tobacco smoke, since in earlier studies structural alteration of collagen was noted by electron microscopy examination, and chemical denaturation of collagen and elastin has been reported in independent studies.[37]

The two studies cited above indicated, to summarize, that exposure to either NO_2 or O_3 does not impair formation of pulmonary alveoli in the growing animal.

Another study examined the morphologic features of experimentally-induced emphysema by NO_2 and papain exposure and compared them with natural emphysema in horses and human beings.[38] This study showed that the NO_2-induced lesion had a "stretched" appearance, rather similar to the natural disease and that thepapain lesion had a flaccid, "motheaten" appearance. A notable finding of this study was that the physical appearance of emphysema varied with the species studied and was possibly influenced by differences in the size and frequency of the inter-alveolar pores (pores of Kahn) graded as follows:

Horse	27.13
Monkey	8.50
Man	6.14
Hamster	3.64
Mouse	3.08
Rat	1.28

In this study emphysema was shown to be induced in mice after continuous and intermittent exposure to 100 $\mu g/m^3$ (0.5 ppm) NO_2.

A study was conducted to look at the possible interaction of NO_2 and O_3 by the parameter of induced pulmonary lesions. Since these two gases occur at approximately equal concentrations on a ppm basis in ambient air, various exposures were carried out with equal parts of the two gases. The lesions described were qualitatively similar. Desquamative Type I lesions and replacement by Type II occurred at 0.25 ppm O_3, but required 10-20 times this amount for NO_2 to elicit similar lesions. Thus, the NO_2 effect was obscured when equal parts of the gases were employed. Equivalent concentrations needed to produce equal lesions were on the order of 0.5 ppm to 0.9 ppm O_3 and 15-20 ppm NO_2. Effect was noted at 0. 5 ppm O_3 after 24 hours exposure.[39]

5.1.2.2.1.2 Biochemical effects of NO_2--The biochemical mechanisms by which NO_2 reacts with tissue resemble O_3 to some degree by virtue of their common oxidizing properties. Thus, lipid peroxidation has been

Table 5.7. SUMMARY OF DATA FOR RATS IN MORPHOMETRIC STUDY[36]

	Ozone (20)	Control (17)	P
Initial Body Wt. (gm)	87.6 ± 1.2	87.0 ± 1.4	N.S.
Final Body Wt. (gm)	284.8 ± 4.8	291.4 ± 4.5	N.S.
Wet Lung Wt. (gm)	1.80 ± 0.03	1.80 ± 0.03	N.S.
Dry Lung Wt. (gm)	0.438 ± 0.008	0.444 ± 0.011	N.S.
Lung Volume (ml)	9.28 ± 0.37	7.97 ± 0.41	<0.02
Mean Chord Length (μ)	62.5 ± 0.7	59.5 ± 0.8	<0.01
Alveolar Surface Area (cm^2)	6786 ± 242	6102 ± 247	<0.05
Alveolar Number (millions)	39.7 ± 1.4	37.8 ± 2.3	N.S.

Mean values ±1 S.E. for 10 Ozone and 17 Control animals.
N.S. = no significant ($P>0.05$)

reported both from in vivo and in vitro exposure to NO_2. Exposure of rats to 1 ppm NO_2 produced evidence of peroxidation as apparent from the appearance of diene conjugates of polyunsaturated fatty acids in extracts of lung lipids, as described by Thomas et al.[40] Peroxidation was maximal 24 hours after exposure and persisted for at least 48 hours after exposure. When exposure consisted of six daily four-hour exposures, the diene conjugates increased cumulatively.

As with ozone, animals receiving a tocopherol-deficient diet have been found to be more susceptible to lipid peroxidation. According to these authors, reactions differ from ozone, at least in their thin films, in that phenolic antioxidants retarded NO_2 but had little or no effect on ozone. The authors speculate that the NO_2-catalyzed reaction proceeds indirectly by the formulation of a nitroso free radical, citing

Table 5.8. NUMBER OF PARENCHYMAL AIR-SPACE UNITS (ALVEOLAR AND DUCTAL), RATES OF FORMATION, AND INDIVIDUAL VOLUMES IN THE MATURING CONTROL AND NO_2-EXPOSED RAT LUNGS[35]

	Number of Parenchyman Air-Space Units			Volume of Individual
Age (Days)	Per Unit Volume ($x\ 10^3$)	Per Whole Lung ($x\ 10^3$)	Formed Per Day ($x\ 10^3$)	Air-Space Units (ml $x\ 10^{-5}$)
		Exposed to Air		
1	20.9	5.6	3.2	4.8
4	20.0	16.2	7.4	5.0
10	54.6	60.4	5.7	1.8
15	62.2	89.1	3.7	1.6
25	54.4	126.3		1.8
40	98.3	230.0		1.0
50	68.3	214.8	1.9	1.5
60	43.7	224.0		2.3
75	35.3	224.9		2.8
		Exposed to About 15 ppm NO_2 in Air		
1	28.3	8.9	2.4	3.5
3	25.3	13.7	2.1	3.9
10	31.0	28.5	5.0	3.2
20	34.1	78.2		2.9
35	26.5	93.0	2.6	3.8
55	28.6	196.8		3.5
75	31.2	223.3		3.2

the work of Estefan et al.[41] The nitroso free radical, in turn, initiates auto-oxidation by the abstraction of methyl hydrogen. The alkyl free radical then reacts with molecular oxygen-forming fatty acid, hydroperoxide, leading to peroxidation reaction in a normal manner. Antioxidants thus prevent NO_2 catalyzed by reaction with the peroxy free radicals.

The ozone-catalyzed reaction proceeds by the direct addition of O_3 across the fatty acid double-bond. These differences may explain the lower toxicity of NO_2 as compared to ozone. The autocatalytic reaction induced by NO_2 might be expected to produce a low development of the products of initiation followed by a rapid reaction once critical concentration was achieved. Thus, normal cellular protective mechanisms, such as the antioxidants, may extend this period more or less indefinitely, unless an overwhelming concentration of NO_2 is employed, whereas for ozone, direct attack on the fatty acid double-bond would not be autocatalytic and repair forces would be ineffective. Thus, the phenolic antioxidants would be ineffective in blocking the reaction.

Studies by Buel, et al.[42] suggest that exposure to NO_2 may alter the molecular structure of lung collagen. When animals were subjected to one exposure, the reaction appeared reversible, but animals exposed to 0.25 ppm repeatedly showed persistent structural alterations when viewed by electron microscopy. These changes persisted for at least seven days after the final exposure. Considerable attention has been paid to the ability of NO_2 to cause alterations in blood or tissue enzymes. Buckley and Balchum[43-45] have described the influence of acute and chronic exposure to NO_2 on the total activity of lactic dehydrogenases (LDH) and on the proportion of its various isoenzymes. Briefly, exposure for 10 weeks or longer at 10 ppm or two hours at 40 ppm caused changes both in tissue oxygen consumption and LDH and aldolase activity. They noted also that a shift to the anaerobic isoenzyme occurred in the lung. Ehrlich[46] also noted this anaerobic shift in the heart muscle of exposed hamsters, and Sherwin et al.[47] noted that hyperplastic epithelial cells formed in response to NO_2 exposure stained heavily for LDH and suggested the demonstration of these cells by histochemical technique might be a useful index of exposure. This increase in number of LDH positive cells was also noted by Buckley and Loosli[48] after exposure of germ-free mice to NO_2.

The significance of the above findings is unclear, since the high levels of exposure may have produced artifactual response. However, recent unpublished and unconfirmed data suggest that a number of blood and tissue enzymes may be altered in guinea pigs by intermittent exposure for four months at levels as low as 0.5 ppm. These data urgently need confirmation since their implications for biological effects of NO_2 are evident.

The striking difference in methemoglobin generation between _in vitro_ and _in vivo_ exposure of blood possibly may be accounted for by the activity of methemoglobin dysmutase, which causes a rapid reversal to oxyhemoglobin in the intact animal, and that during actual exposure by inhalation, the conversion to methemoglobin does not exceed the power of this enzyme to effect the reversal to oxyhemoglobin.

Two biochemical studies currently are being conducted. The first examines the prospect that the toxicity of NO_2 and O_3 may be an "ultimate" toxicant produced by a reaction between theoxidant and unsaturated fatty acid. Ozone is known to react with unsaturated fatty acids to produce fatty acid ozonides. Fatty acid ozonides produce Heinz bodies in human and mouse erythrocytes. Heinz body formation is inhibited in human red cells by supplementation with Vitamin E. This property is responsive to Vitamin E as is the inhalation toxicity of O_3 in animals. The same pathways are likely to occur in animal models as in man if fatty acid ozonides are the true toxicant. Fatty acid ozonides also produce lung edema. If fatty acid ozonides produce the same anatomical lesions in the lung as O_3 inhalation, one could suppose that ozonides manufactured on inhalation are the responsible agents. NO_2 similarly can react with unsaturated fatty acids to produce nitroxide fatty acids which have an unpaired electron and are likely to be very reactive. No data are available on their properties, but nitroxide fatty acids could likewise be the "ultimate" toxicant on NO_2 inhalation.[49-52]

These studies are important because:

(1) Identification of the chemical mediators of intoxicant ion allows a rational approach to estimation of health hazards and preventative measures;

(2) In vitro systems can be used to accelerate studies of long-term exposure;

(3) Indicators of human exposure may be possible by measuring blood levels of the "ultimate" toxicant, a by-product or an alteration of a blood cell population (Heinz bodies in red cells, numbers of polyphonuclear cells or modifications of platelets);

(4) The occurrence of systemic effects from NO_2 or O_3 inhalation (such as carcinogenesis, mutagenesis, impaired liver function or splenomegaly) may be predicted; and

(5) Animal exposure effects may be related better to human effects, refining data for criteria and standards.

Progress to Date: Methyl oleate ozonide has been synthesized and purified. Methods of rat lung fixation for electron microscopy have been established by either perfusion of the vascular system or by intratracheal instillation. The former appears most useful for observations of the alveolar surface while the latter appears best for general anatomical surveys. A method of imbedding which orients macroslices at the light microscopic level has been applied to the lung. Studies are focused on the terminal bronchiole-alveolus region which has been shown by Freeman's group to be the most sensitive area of the lung to NO_2 or O_3 inhalation.

Synthesis of the ozonides of all of the remaining common unsaturated fatty acids (linoleic, linolenic and arachidonic acids) is planned. Studies of methyl oleate ozonide effects on the lung (using intraperitoneal and intravenous injection) are under way. Lungs will be examined by the two methods to assess morphological changes at the alveolar surface and the pneumocyte-capillary interchanges caused by O_3 inhalation. The dose-response relationship for ozonides will be compared with O_3 inhalation to estimate the in vivo conversion of fatty acids to ozonides.

Nitroxide fatty acids will be synthesized and used as above to determine the similarities and differences between NO_2 inhalation and nitroxide fatty acid toxicity. The conversion to nitroxide fatty acids on NO_2 inhalation will be estimated as for O_3 by comparative toxicities using parallel-line bioassay. These observations and those for O_3 will be compared to determine if a similar mechanism of action exists.

Because these studies relate to mechanistic observations, future studies are likely to involve the systemic effects of long-term exposure on cells other than penumocytes. Potential mutagenic and carcinogenic properties are now known, but likely, since these compounds appear to act on the cell surface by free radical generating mechanisms. The co-carcinogenic potential is marked since they are likely to interact with microsomal oxygenases which are known to produce the ultimate carcinogens of chemical carcinogenesis. The properties of these ultimate carcinogens, arene oxides, are similar to fatty acid ozonides. Co-carcinogenesis studies using the Saffiotti hamster tracheobronchial tumor induction model and ozone exposure are under way in-house at this time.

The second biochemical study examines the mechanism of action of of nitrates and sulfates--The purpose of these studies is to determine if vasoactive compounds are released from the lung by SO_2 or sulfate, or NO_2 or nitrate. Since SO_2 inhalation results in bronchiocon-triction below the begal reflex, it is likely that direct action on the bronchial smooth muscle is involved. Histamine aerosols produce effects very similar to SO_2 inhalation. Sulfate particulates have been suggested by the CHESS studies to be better correlated with human effects than SO_2 *per se*. The effects of sulfate as a modulator or releasing agent of vasoactive compounds from an *in vitro* model system were therefore studied.

Using guinea pig lung slices because of their supposed similarity to human lung, histamine was found to be released by sulfate ions in the presence of ammonium ion. Nitrate ion produced some release also but ammonium ion is a requisite for release of histamine. Histamine release was not due to ionic artifacts. By the use of $^{35}SO_4$ ion uptake of sulfate was found to occur simultaneously with histamine release. Sulfate uptake was found to be intracellular. Ammonium ion decreased sulfate uptake simultaneously with histamine release, suggesting that histamine release occurred either by cell lysis or by degranulation of lung mast cells. Sulfate effects were not blocked by pharmacological agents such as adrenergic or cholinergic drugs nor by cyclic-AMP or GMP.

These studies suggest that sulfate can act directly upon the lung mast cell to cause histamine release. Sulfate requires ammonium ion for effect. (Table 5.9) Sulfate particulates are principally associated with ammonia, but ammonium ion could be supplied from the blood. The potentiation of sulfate effects by ammonia may explain the toxicity of these aerosols over SO_2. Ammonium ion probably exerts this effect by acting as a proton sink within the cell. Sulfate is probably transported by the chloride ion carrier. Inhibitors of chloride transport such as phloritin are being investigated.

An important result of these in vitro studies is that the ammonia concentration of the inhaled mixture may cause substantial changes in toxicity studies in animals. Ammonia arises from the action of gut bacterial urease on urea in the gut. The second generation catalytic converters deliver ammonia by the incomplete reduction of NO_x. Ammonium

Table 5.9. RELEASE OF HISTAMINE FROM LUNG FRAGMENTS IN THE PRESENCE OF 100 mM SALT SOLUTIONS[49-52]

Compound	No. of Experiments	Histamine Release (μg/gm lung)	Percent Total Histamine Released	Relative Potency* (%)
Sodium Chloride	6	0	0	0
Sodium Sulfate	6	0	0	0
Ammonium Chloride	9	9.4 ± .8	34.8	35.7
Ammonium Acetate	4	15.5 ± .3	57.4	58.9
Ammonium Nitrate	5	15.7 ± 1.3	58.1	59.7
Ammonium Sulfate	6	26.3 ± 1.2	97.4	100.0

*Ammonium sulfate was arbitrarily assigned a value of 100%, since it released approximately 100% of the histamine stores.

sulfate may therefore result and be more toxic than sulfate or sulfuric acid alone.[53]

Sulfate and possibly nitrate is likely to cause the release of histamine by competing for histamine binding sites on heparin in the histamine granule of the mast cell. Rat peritoneal mast cells will be used to isolate mast cell granules in studies planned to investigate this possiblity. Sulfate release of histamine and binding to granule heparin will be measured using acridine orange metachromasia. The release of other vacoactive compounds by sulfate from lung slices will be examined. Prostaglandin synthesis and release will be measured by radioimmunoassay and smooth muscle bioassay. Slow reacting substance of anaphylaxis (SRS-A) release will also be measured by guinea pig ileum assay.

SRS-A has been suggested to be a sulfate ester. In later studies, the incorporation of $^{35}SO_4$ into SRS-A and other substances will be measure to determine if sulfate inhalation stimulates vasoactive hormone synthesis. Sensitized guinea pigs will be used to repeat the sulfate studies above to determine the effect of sulfate on atopic-lik release of vasoactive hormones. Sensitized animals are models of asthmatic individuals. An important mechanism for sulfate effects which could influence all hormone action is the sulfation of the enzyme adenyl cyclase. Adenyl cyclase controls almost all hormone action in the cell. Phosphorylation of the enzyme has been proposed as a control mechanism. Sulfate could compete for this reaction leading to a sulfo enzyme which could be more stable than its phosphorylated counterpart.

A reduction in adenyl cyclase levels could have broad effects. The effect of sulfate on membrane adenyl cyclase will therefore be determined.

5.1.2.2.1.3 Pulmonary physiology--Few studies on the pulmonary physiologic effect of NO_2 have been reported. The subject was thoroughly reviewed in the NATO document.[19] A small amount of activity on the pulmonary physiologic effect with nitrate will take place under the EPA sulfate research program, rationale being the possible similar irritant action of nitrate and sulfate ions and their respective acids, and the fact that the chemicals occur generally in the same polluted atmospheres. Work will proceed on this project commensurate with allocated resources on the basis of pulmonary physiologic response of nitrates and nitric acid mist together with sulfate and sulfuric acid, evaluation of the influence of the ammonium ion. With the present allotment of effort, work should be completed on the relative irritant action of one nitrate by July, 1975.

Studies which employ the interaction of pathogenic organisms and air pollutants to demonstrate increased susceptibility to infectious pneumonia are unique to the EPA program. This sytem has been efficiently utilized in environmental toxicological studies of ozone,[54,55] nitrogen dioxide,[56] irradiated auto smog[57] and exposures to trace metals such as NiO, MnO_2.[58,59] It has been shown that the role of infectivity can be enhanced in mice,[55,56,58,59] rats,[60] hamsters[56] and squirrel monkeys.[61] Among the infectious agents eliciting this reaction in the above animals are Streptococcus pyogenes. Klebsiella pneumoniae, Diplococcus pneumoniae, and influenza PR-8 virus. Thus, this model is an exquisitely sensitive indicator of biological effects in vivo. In addition, the model is useful in studying the mechanism of action of the pollutants.[62,63]

An important problem in the toxicity of NO_2 (and ozone) concerns the relative toxicity of the mode of dose since both of these gases are subject to intermittent diurnal peaks whose frequency and magnitude reflect the input into the atmosphere of NO and other precursor substances, and conditions favoring the formation of the secondary pollutants (photochemical smog). Thus, the population in any given area is not subject to a continuous dose of pollutant, but a series of peaks and valleys of variable duration and irregular occurrence. Previous biological studies have never concertedly attacked this problem and since the import is obvious to heatlh standard-setting and control measures, EPA is making a serious study of the problem. A portion of this program is incorporated into the US-USSR Agreement on Cooperation in the Field of Medical Science and Public Health. Manuscripts are in preparation for presentation in Riga in the USSR in December, 1974,[64] for the above program and in New Zealand at the Australia/New Zealand Clean Air Conference in February, 1975.[65] The principal parameter employed at this state to evaluate the important of mode of dose is the infectivity system described above. A brief review of this information follows.

Figure 5.1 shows greater mortality from pulmonary infection resulting from the same concentration X time for exposure to NO_2 over different time periods. Note that the actual concentration has more influence than duration of exposure. If no interaction existed between concentration and time (i.e., if they had equal importance), all the test groups should show the same mortality in the above experiment--15%. But the trend of the combined data indicates a gradient response from a high of approximately 50% to a low mortality equal to controls.

The interaction of a constant concentration with time over a longer period was examined. Two concentrations of NO_2 have now been studied. A level of 3.5 ppm was used for comparison with the study mentioned above. A lower value of 0.5 ppm was selected since this concentration represented the lowest figure in the published literature showing positive results for chronic exposure in the infective system.[46] The data shown in Figure 5.2 represent 60 individual observations for the 3.5 ppm level and eight observations for the 0.5 ppm. The simple linear regression shows that mortality increased with time and concentration and was statistically significant at the 0.01 probability level. Predictions that can be generated from these regressions show that statistically significant difference from controls occurred after one-hour exposure to 3.5 ppm and after three weeks at the 0.5 ppm concentration. While the first series of experiments (Figure 5.1) showed that there was a strong interaction in favor of concentration over time, the latter study still shows the importance of toxicological information from long-term exposures for NO_2.

The data from the same series of experiments was analyzed for influences of exposure time to 3.5 ppm on mean survival period calculated according to the equation:

$$MST_d = \frac{(A+B) = (d=L)}{n}$$

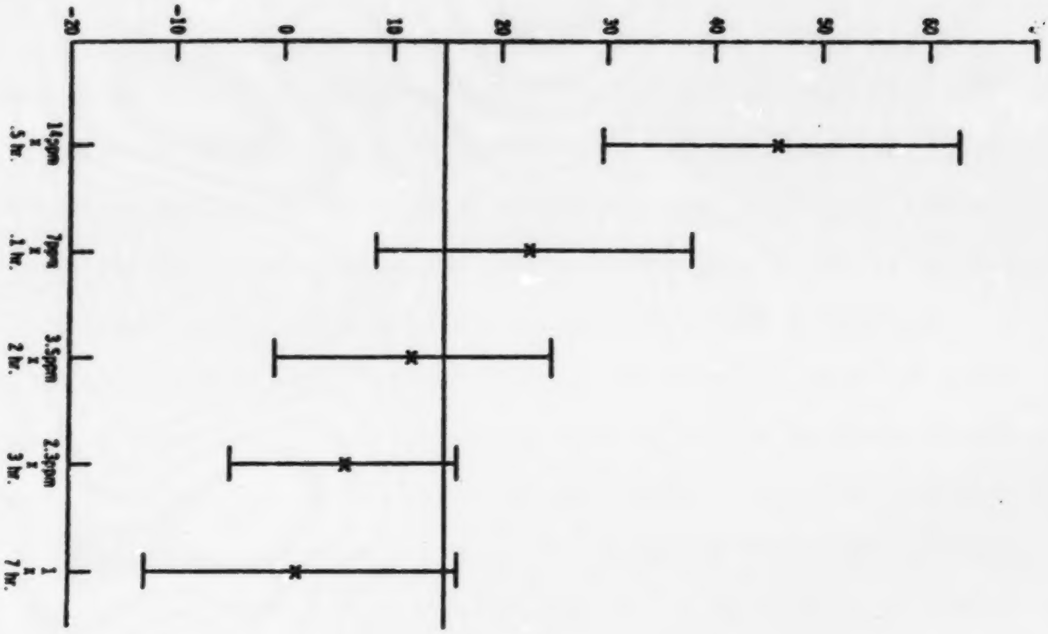


Figure 5.1. % difference in mortality (NO_2 - control)[64]

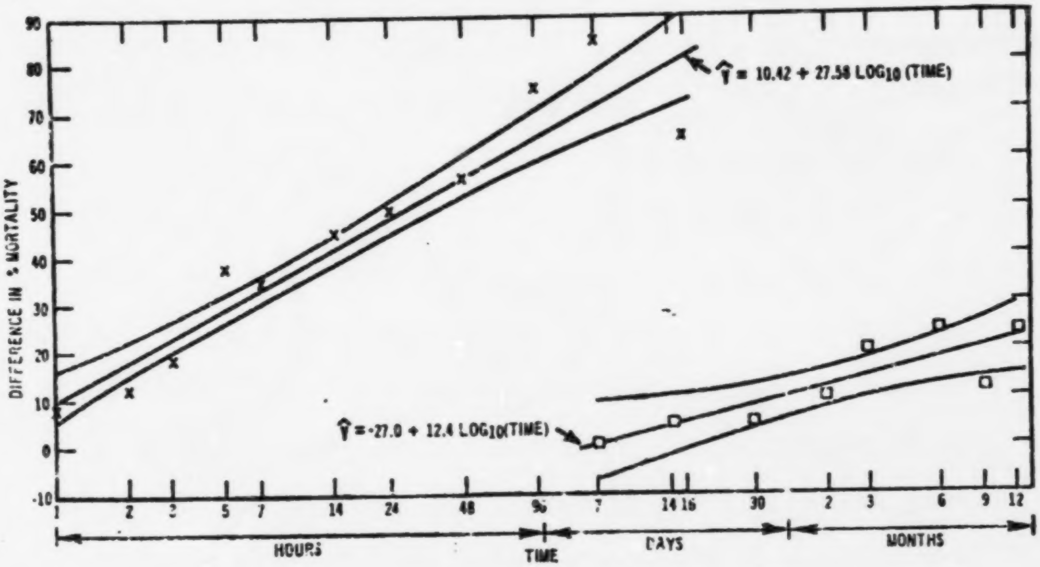


Figure 5.2. Difference in % mortality versus length of exposure to .5 or 3.5 ppm NO_2[64]

"A" is the last day that any individual mouse was alive; "B" is the number of mice surviving "A" days; "D" is the last day of the experiment (in this case 15); "L" is the number of mice that were alive on day "D" and "n" is the initial number of mice in the experimental group.

A statistically significant ($P<.05$) regression with a negative slope was shown for mean survival of mice challenged with Streptococci versus length of exposure to 3.5 ppm for various periods prior to the challenge. Figure 5.3 shows that there is an inverse relationship between survival and length of exposure at constant concentration. With this parameter, effects were also statistically significant after one hour of exposure to 3.5 ppm.

Using the same model system (fixed concentration versus time), other concentrations are now being tested for the purpose of developing information that can be used to develop regression curves at other concentrations. That can then be used for predicting purposes.

Other experiments are also designed to test interaction of concentration and time as above, but they use an intermittent exposure model in place of continuous exposure. As this report is being prepared, data from this experiment is still being collected.

5.1.3 Carbon Monoxide

5.1.3.1 Human Studies--The present ambient air quality standard for carbon monoxide [10 $\mu g/m^3$ (9 ppm) averaged over eight hours and of 40 $\mu g/m^3$ (35 ppm) one hour average] produces carboxyhemoglobin levels of approximately 1.5%. Since the time of establishment of the standard, new evidence has appeared giving additional support to the current standard in three areas. These are: (1) Effects on individuals

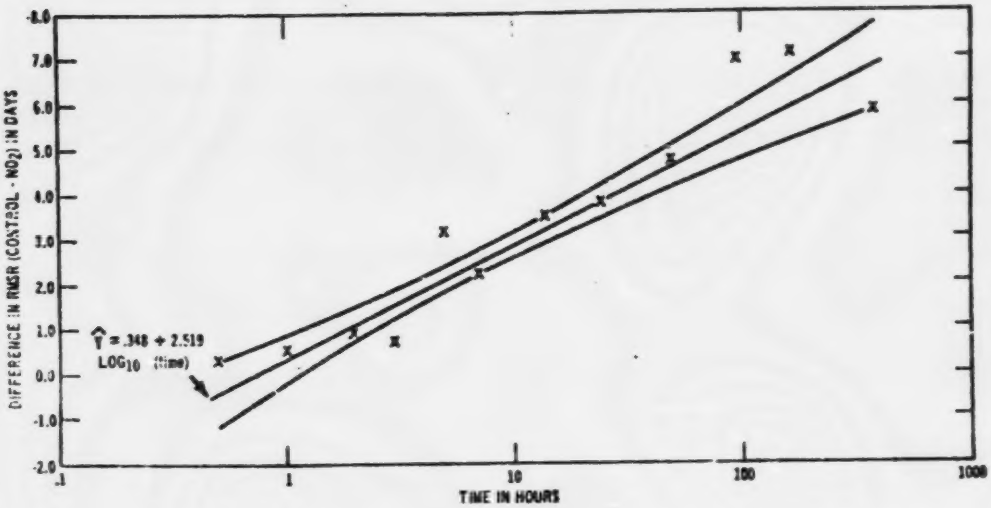


Figure 5.3. The difference in mean survival time between control of NO$_2$ mice versus length of exposure to 3.5 ppm NO$_2$[64]

with atherosclerotic vascular disease, (2) efffects on exercise capacity in healthy individuals and (3) additional evidence on alertness effects.

5.1.3.1.1 Effects on individuals with Cardiovascular disease--Three separate studies[66-68] have shown that individuals with atherosclerotic heart disease manifested by angina pectoris experienced chest pain earlier during exercise when carboxyhemoglobin concentrations are in the 2.5-3.0% range than when they are about 1.0%. Another study[69] has shown that men with peripheral atherosclerotic disease develop leg pain after less walking at carboxyhemoglobin levels of 3.0%. These studies were well controlled and demonstrate increased morbidity in a segment of the population with a common disease process.

5.1.3.1.2 Effects on exercise--Young, healthy men at carboxyhemoglobin concentrations of 5.0% have increased heart rates and decreased maximal oxygen consumption when undergoing strenuous exercise.[70] Preliminary analysis of an EPA study indicated lessened exercise performance at COHb levels of approximately 5-6%.[71]

Decrements in exercise capability in the healthiest segment of the population suggest more serious impairments in older persons who frequently have subclinical cardiovascular disease.

5.1.3.1.3 Effects on alertness--Several recent studies have shown impairments on vigilance tasks at carboxyhemoglobin concentrations ranging from 3.0-6.5%.[72-74] These data tend to support the original neurobehavioral work used to set the standard.[75]

Other evidence has appeared in recent years implicating levels of carboxyhemoglobin below 10% with increased risk of atherosclerosis,[75] impaired fetal development[76] and in altered drug metabolism.[77] While this evidence is certainly inconclusive at present, it still indicates the range of pathophysiologic functions possibly affected by carbon monoxide and the need for additional research.

The strongest evidence now supporting the present standard rests on the harmful effects of CO on individuals with cardiovascular disease. Cardiovascular disease is widespread among adults and present studies indicate aggravation of symptoms in a large sub-set of these adults.

The ambient standard is given in Table 5.10. Table 5.11 gives the judgment threshold estimates for health effects of CO. Values are given for CO concentrations at light activity and during exercise as well as rest since equilibration with a given CO concentration occurs more rapidly with increased ventilation. Table 5.12 gives the estimated size of the population at risk from adverse effects of carbon monoxide.

Table 5.10. AMBIENT AIR QUALITY STANDARD FOR CARBON MONOXIDE

Pollutant	National Primary Standard	
	Concentration (mg/m^3)	Averaging Time
Carbon Monoxide	10 (9 ppm)	Maximum 8-hour
	40 (35 ppm)	Maximum 1-hour

5.1.3.2 Animal Studies--Apparently no animal experiments have been conducted since publication of Air Quality Criteria for Carbon Monoxide (1970) that employed <50 ppm CO exposures. This concentration was the lowest exposure level reported in that document. The emphasis since 1970, however, has shifted from reporting ambient concentrations to reporting carboxyhemoglobin (COHb) levels and the relationship of the parameter with the effects.

New data from animal experiments reported since publication of the 1970 criteria document have shown that COHb levels as low as 2% in animals decrease pO_2 of brain and liver. Dogs were previously reported to show blood changes at 7.3% COHb, but newer data shows that 5% COHb increases coronary blood flow. COHb levels of 9-10% maintained in rabbits during half of the gestation period resulted in decreased birthweight and increased neonatal and infant mortality.

Zorn[78] studied the effects of CO inhalation on the brain and liver pO_2 of animals using Lubber's platinum electrode and surface electrodes. In both tissues the pO_2 decreased, even at carboxyhemoglobin of 2% saturation and the decrease varied approximately linearly with the increase in COHb.

Table 5.11. JUDGMENT THRESHOLD ESTIMATES FOR HEALTH EFFECTS FOR CO

Adverse Health Effects	COHb at which effect was observed	Equivalent 8 hour CO exposure (mg/m^3)			Equivalent 1 hour CO exposure (mg/m^3)		
		Rest	Light Activity	Exercise	Rest	Light Activity	Exercise
Impaired Exercise Tolerance in persons with cardiovascular disease	3.0%	29	24	23	143	90	73
Decreased physical performance in normal adults	5.0%	50	41	39	355	223	179
Interference with mental activity	5.0%	50	41	39	249	156	125
Increased risk of atherosclerosis	insufficient evidence						
Impaired fetal development	insufficient evidence						
Altered tolerance to common drugs	insufficient evidence						

Table 5.12. SIZE OF POPULATION AT POTENTIAL RISK OF POLLUTANT INDUCED EFFECT

Adverse Health Effect	Expected Frequency of Adverse Effect Population (rate per 100)	Potential Size of Population at Risk*
Impaired exercise tolerance in persons with heart disease	5% of adults (18 years and above)**	4.2 million
Decreased physical performance	100%	140 million
Interference with mental activity	100%	140 million

*Assumes a U.D. population of 200,000,000, 70% of which lives in urban areas of increased pollution.

**1960-1962 Health Examination Survey, U.S.P.H.S.

A second study by Rondia[79] found that there was a decreased ability of rat liver to metabolize 3-OH benzon alpha pyrene in rats exposed to 60 ppm CO.

Coburn and Kane[80] studied COHb concentration of 10-12% in anaesthetized dogs and found that this concentration resulted in an inhibition of loss of hemoglobin-haptoglobin from the plasma. Researchers studying the relationship of varying concentrations of COHb and increased coronary blood flow exposed conscious dogs to CO at increasing concentrations and observed a 13% increase in coronary blood flow with a 4% increase in COHb.[81] At 20% COHb coronary blood flow increased by 54%. Coronary flow measurements at 4 COHb concentrations suggested a linear relation between COHb concentration and flow. A threshold value was not observed, although measurements were not made below 5% COHb.

COHb levels chronically increased to an average of 12.4% in cynomolgus monkeys produced polycythemia with an increase in hematocrit from 35-50% volume of packed cells.[82] All animals developed increased amplitude of P-wave in the EKA, and some developed T-wave inversions suggestive of myocardial ischemia. Monkeys with experimental myocardial infarction had higher COHb and more severely abnormal EKG than normal monkeys or monkeys with myocardial infarction breathing room air.

Wells[83] studied pregnant rats exposed to 15,000 ppm (1.5%) for 5-8 minutes 10 times every other day during 21-day pregnancy and found maternal unconsciousness and abortion or resorption absorption in most of the fetuses. The surviving newborns did not grow normally. No pathologic changes in nervous system were noted. Similar exposure to 5900 ppm affected only a small portion of the animals.

Williams and Smith[84] exposed rats to CO at 3400 ppm for one hr/d for three months. Peak COHb = 60 = 70%; of seven exposed females, half the control number pregnancies occurred. The number of young delivered decreased and only 2/13 newborns survived to weaning. In five females exposed for five months, no pregnancies occurred.

Astrup et al.[77] studied pregnant rabbits exposed to CO of 90 ppm for 30 days. Exposure during first pregnancy resulted in COHb 9-10%. Birthweights decreased 12%. Neonatal mortality increased from 4.5% in controls to 10% in exposed. Mortality during the following 21 days increased from 13-25%.

In a second experiment, pregnant rabbits were exposed to CO of 180 ppm for 30 days. Exposure during first pregnancy resulted in COHb 16-18%. Birthweights decreased 17%, neonatal mortality 35% vs. 1% and mortality in following 21 days was 27% vs. same in controls.

Baker and Tumasonis[85] exposed chicken eggs to various concentrations of CO 0-650 ppm continuously from laying through 18 days of incubation and found that hatchability was inversely related to [CO]. 425 ppm reduced hatching to 75%, embryo weight was normal, no congenital abnormalities, 650 ppm reduced to 46% and developmental anomalies of tibia and metatarsal bones.

Baker et al[86] also exposed eggs 12 and 17 days old to CO of 425 ppm for 24 hours. COHb in 18-day-old chicks averaged 36%. Livers of 18-day-old chicks had about 50% increase in the activities of two hepatic mixed-function oxidases, hydroxylase and O-demethylase. No effects were seen on 13-day-old chicks.

McGrath and Jaeger[87] found that 50% of newly hatched chicks withstood exposure to 10,000 ppm for 32 minutes. Survival time to this [CO] decreased with postnatal age from 10 minutes in one-day-old chicks to four minutes at ages 8-21 days.

Jones[88] exposed rats, guinea pigs, monkeys and dogs to 51, 96 and 200 ppm for 90 days and found no toxic effects of the CO. The only reported physiological change was increased hemoglobin and hematocrit values for all species.

Ator[89] exposed rats to 100-1000 ppm of CO for 90 minutes and found no effect on response rate for differential reinforcement of low-rate schedules at exposures up to 250 ppm.

Gage et al.[90] found significantly higher activity in female mice exposed to 100 ppm CO for four-seven days than in males similarly exposed or in female controls. No statistically significant effect on the activity of male mice occurred under these exposure conditions.

5.1.4 Hydrocarbons

The National Ambient Air Quality Standard for hydrocarbons was based almost entirely on their role as precursors of other compounds formed in th- atmospheric photochemical system and not upon direct effects of the hydrocarbons. Particulate hydrocarbons and more specifically polynuclear hydrocarbons were not considered on the criteria document. Ambient air data are limited primarily to non-methane gaseous hydrocarbons and benzo-a-pyrene.

The National Academy of Sciences published a review on particulate polycyclic organic matter in 1972.[91] A scientific and technical assessment report by EPA on the same subject is in the final stage of publication. EPA reports on polychlorinated biphenyls and vinyl chloride are also in the final stage of publication.

Aksoy et al.[92] has reported on six cases of Hodgkin's disease in workers with a history of chronic benzene exposure. The subjects were exposed to benzene for a period ranging from 1 to 28 years with a mean of 11 years before the onset of Hodgkin's disease. The concentration of benzene in the working environment ranged between 150 and 210 ppm. Ventilation in the work places was reported as poor. A summary of these cases is shown in Table 5.13. There was no indication in this report of the number of workers at risk or any discussion of other possible agents that might have been present in a poorly ventilated work place.

Ahmad and Whitson[93] reported on one incidence of rapid loss of consciousness of 10 new female employees reporting for work in an industrial garment company. Immediately after the incidence, measured concentrations of formaldehyde ranged from 2 to 10 ppm. Other workers in the area had no apparent difficulties. The authors suggest that the response was due to exposure to formaldehyde although little additonal evidence was given.

Thorpe[94] conducted a study of eight affiliates engaged in the manufacture, transportation and marketing of petroleum or chemical products containing benzene for at least 10 years. The incidence of leukemia in the general population with an age distribution similar to that in the Thorpe study is about three to eight cases per 100,000 population. Eighteen cases of leukemia were reported for the period 1962 to 1971. These cases were distributed among four of the affiliates--the other four reported none. A summary of the 18 cases is shown in Table 5.14.

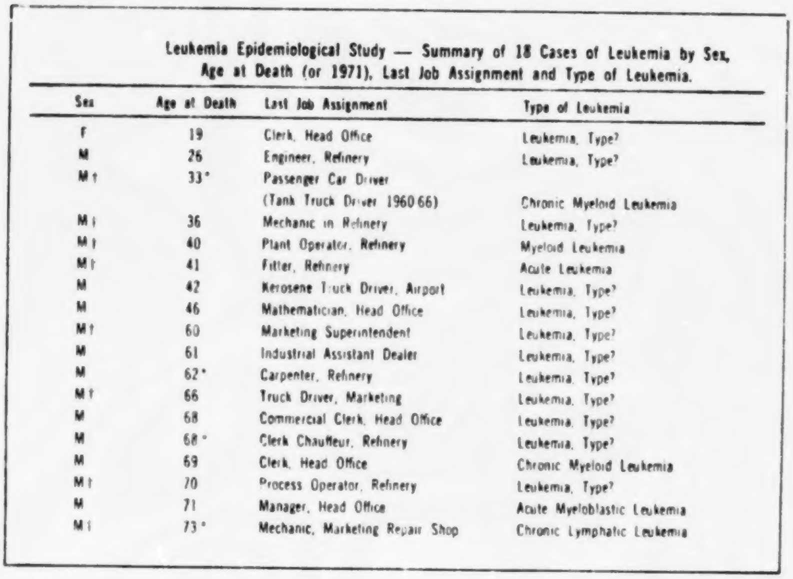
Thorpe also found that the occurrence of leukemia in a population of 38,000 working in a variety of petroleum and petrochemical operations, some of whom were exposed to low levels of benzene over a 10-year period, was not abnormal compared to the general population in the countries concerned (see Table 5.15). As pointed out by Thorpe, there were problems with the data base and a number of important assumptions were necessary.

Table 5.13. SOME CLINICAL HEMATOLOGIC AND PATHOLOGIC FINDINGS IN SIX PATIENTS WITH HODGKIN'S DISEASE

Case	Age Sex	Occupation	Duration of symptoms befor adm.* (months)	Duration of exposure (years)	Symptoms	Signs	Some laboratory findings	Pathologic findings	Stage
1	61 M	Compass repairman	8*	28	*Pel-Ebstein* fever	Cervical, inguinal lymphadenopathies hepatosplenomegaly	WBC 4200, lymphopenia, ESR: 149 mm./hr.	Mixed cellularity	IV
2	39 M	Shoemaker	1	10	*Pel-Ebstein* fever	Both inguinal, cervical, axillar lymphadenopathies, moderate hepatosplenomegaly	WBC 5400, lymphopenia, ESR: 82 mm./hr.	Mixed cellularity	IV
3	31 M	Shoemaker	7	6	*Pel-Ebstein* fever, Pruritis	Both cervical, inguinal, axillar lymphadenopathies, moderate hepatosplenomegaly	WBC 2800, severe lymphopenia, ESR: 62 mm./hr.	Lymphocytic depletion	IV
4	30 M	Car painter	8	11	Fever	Cervical, axillar lymphadenopathies findings of liver cirrhosis	WBC 5800, lymphopenia, ESR: 118 mm./hr.	Mixed type	IV
5	50 M	Shoemaker	2	10	Weight loss	Both cervical, axillar, inguinal, lymphadenopathies involvement of tonsils	WBC 11600, no lymphopenia ESR: 37 mm./hr.	Lymphocytic predominance	III A
6	27 M	Television repairman	1	1	Fever	Cervical and mediastinal lymphadenopathies	WBC 10800, lymphopenia, ESR: 97 mm./hr.	Mixed type	II B

* Ad.: admission.

Table 5.14. LEUKEMIA EPIDEMIOLOGICAL STUDY



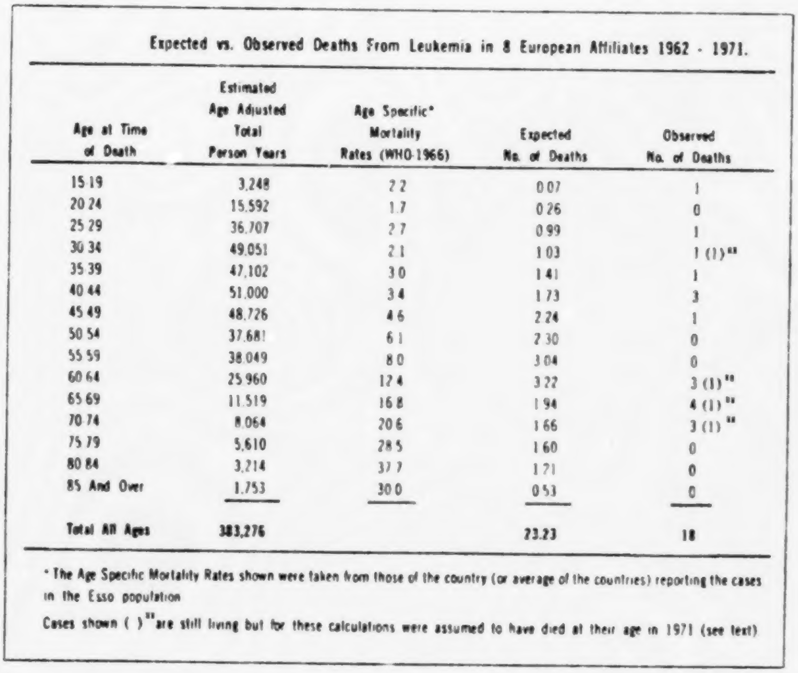
Leukemia Epidemiological Study — Summary of 18 Cases of Leukemia by Sex, Age at Death (or 1971), Last Job Assignment and Type of Leukemia.

Sex	Age at Death	Last Job Assignment	Type of Leukemia
F	19	Clerk, Head Office	Leukemia, Type?
M	26	Engineer, Refinery	Leukemia, Type?
M †	33 *	Passenger Car Driver (Tank Truck Driver 1960-66)	Chronic Myeloid Leukemia
M †	36	Mechanic in Refinery	Leukemia, Type?
M †	40	Plant Operator, Refinery	Myeloid Leukemia
M †	41	Fitter, Refinery	Acute Leukemia
M	42	Kerosene Truck Driver, Airport	Leukemia, Type?
M	46	Mathematician, Head Office	Leukemia, Type?
M †	60	Marketing Superintendent	Leukemia, Type?
M	61	Industrial Assistant Dealer	Leukemia, Type?
M	62 *	Carpenter, Refinery	Leukemia, Type?
M †	66	Truck Driver, Marketing	Leukemia, Type?
M	68	Commercial Clerk, Head Office	Leukemia, Type?
M	68 *	Clerk Chauffeur, Refinery	Leukemia, Type?
M	69	Clerk, Head Office	Chronic Myeloid Leukemia
M †	70	Process Operator, Refinery	Leukemia, Type?
M	71	Manager, Head Office	Acute Myeloblastic Leukemia
M †	73 *	Mechanic, Marketing Repair Shop	Chronic Lymphatic Leukemia

* Living

† In Exposed Group

Table 5.15. EXPECTED VS. OBSERVED DEATHS FROM LEUKEMIA IN EIGHT EUROPEAN AFFILIATES 1962-1971



Expected vs. Observed Deaths From Leukemia in 8 European Affiliates 1962 - 1971.

Age at Time of Death	Estimated Age Adjusted Total Person Years	Age Specific* Mortality Rates (WHO-1966)	Expected No. of Deaths	Observed No. of Deaths
15-19	3,248	2.2	0.07	1
20-24	15,592	1.7	0.26	0
25-29	36,707	2.7	0.99	1
30-34	49,051	2.1	1.03	1 (1)**
35-39	47,102	3.0	1.41	1
40-44	51,000	3.4	1.73	3
45-49	48,726	4.6	2.24	1
50-54	37,681	6.1	2.30	0
55-59	38,049	8.0	3.04	0
60-64	25,960	12.4	3.22	3 (1)**
65-69	11,519	16.8	1.94	4 (1)**
70-74	8,064	20.6	1.66	3 (1)**
75-79	5,610	28.5	1.60	0
80-84	3,214	37.7	1.71	0
85 And Over	1,753	30.0	0.53	0
Total All Ages	**383,276**		**23.23**	**18**

* The Age Specific Mortality Rates shown were taken from those of the country (or average of the countries) reporting the cases in the Esso population

Cases shown ( )** are still living but for these calculations were assumed to have died at their age in 1971 (see text)

Some polycyclic aromatic hydrocarbons are the most ubiquitous carcinogens known. The noxious effects of tobacco smoke in humans and animals has been attributed to presence of various hydrocarbons. Short-term exposures of guinea pigs to cigarette smoke decreased the number of free lung-cells--macrophages and leukocytes--as determined from lung lavage preparations.[95] The decrease in numbers of macrophages was attributed to the presence of acetaldehyde, tar, nicotine, hydrogen cyanide and acrolein. And the decrease in the number of leukocytes was related to acetaldehyde, tar and pH of the particulate phase.

Confirming the previous observations that toxicity of smoke was part of the vapour phase of the smoke, the above studies also indicate that biologically significant activities exist in the particulate phase of the smoke. Necessary long-term biological experiments are warranted to verify these short-term observations.

The cigarette smoke condensate (CSC) contains aromatic hydrocarbons, such as pyrene, benzo[e]pyrene and benzo-[g,h,i]perylene, that have been considered non-carcinogenic up to now.[96] In addition, CSC also contains phenols, the most important of which is catechol (1,2-dihydroxy-benzene).[97] Attempts to assess the carcinogenic or co-carcinogenic activity of these compounds in CSC on female mouse (1 CR/Ha) skin demonstrated remarkable carcinogenic activity of catechol and the three aromatic hydrocarbons.[98] Each of these produced skin papillomas and squamous cell carcinomas in mice. Catechol also exhibited co-carcinogenicity in these tests. The animals received catechol (2,000 μg), benzo[e]pyrene (15 μg), Pyrene (12 μg) and benzo[g,h,i]perylene (21 μg) per 0.1 ml acetone, three times a week for 52 weeks.

Catechol is found in many plants and trees,[99] including tobacco leaves.[100] Compelling practical problems suggested by this study include immediate need to develop a less harmful cigarette and to reduce or eliminate emissions of hazardous material from tobacco.

Certain chemicals such as chloromethyl methyl ether (CMME) and bis chloromethyl ether (BCME) are widely used as intermediates in organic synthesis and preparation of ion-exchange resins. An increased incident of oat-cell carcinomas were seen (13 or 14 men with lung neoplasms) in men exposed to CMME.[101] Commercial CMME contains 1 to 7% BCME. Both CMME and BCME are highly carcinogenic for mice and rats.[102-105]

Mammalian tissue cultures have been used to study induction of microsomal enzymes because of ease of control of time of exposure and concentration of inducer. Following this lead, human foreskin obtained from infants (two to four days old) at time of circumcision was grown in tissue culture.[106] Such foreskin tissue cultures were exposed to 10 µM of benz-(a)-anthracene (BA) for 16 hours to induce benzo(a)pyrene hydroxylase. This hydroxylase activity was greater (1.78 to 5.30 times) in foreskins treated with BA when compared to the foreskins in the controlled medium without BA.

Considering the size of the skin pool and evidence of inducibility of benzo(a)pyrene hydroxylase in skin, the role of skin in detoxification of various polycyclic hydrocarbons may be significant. The levels of benzo(a)pyrene hydroxylase (BP hydroxylase) in liver and extraphepatic tissues differ markedly from strain to strain of mice. This difference may mean that genetic factors influence the constitutive level and inducibility of BP hydroxylase. As the extra-hepatic tissues in mice are frequently the targets for polycyclic hydrocarbon carcinogenicity, the inducibility of BP hydroxylase in extra-hepatic tissues from mouse strains investigated exhibited 3-methylcholanthrene and 5-6-benzoflavone.[107]

Results from the liver, lung and skin of mice of various strains show that tissues vary in their ability to produce BP hydroxylase in a given strain. The three (3) hydrocarbons above were equally capable of inducing hepatic BP hydroxylase. However, 3-methylcholanthrene was a far less effective inducer of BP hydroxylase in extra-hepatic tissues (lung and skin) than either benz(a)anthracene or 5-6-benzoflavone.

5.1.5 Oxidants

The present U.S. National Primary Standard for photochemical oxidants is 160 $\mu g/m^3$ (0.08 ppm) maximum one-hour concentration not to be exceeded more than once per year.[108,109]

The original evidence for this standard for people included a broad range of morbidity such as aggravation of asthma, aggravation of chronic lung disease, irritation of the respiratory tract in healthy adults, decreased visual acuity, increased eye irritation and decreased cardiopulmonary reserve in healthy subjects. These data were completely reviewed in the original photochemical oxidant criteria document.

Three important papers on pulmonary function after short-term ozone exposure were published during the 1969-1974 period. All three studies were of healthy adults. Bates et al.[110] observed substernal soreness, cough and some phoryngitis and dyspnea along with decreased pulmonary function among healthy, lightly-exercising volunteers experimentally exposed to 1500 $\mu g/m^3$ of ozone for two hours. Hazucha et al.[111] observed similar effects in volunteers exposed to either 1500 $\mu g/m^3$ or 740 $\mu g/m^3$ of ozone for two hours.

Bates[112] reported a marked decrease in pulmonary function among healthy subjects doing light exercise and exposed simultaneously to 740 $\mu g/m^3$ of ozone and 1000 $\mu g/m^3$ of sulfur dioxide for two hours. This deleterious effect may be synergistic and a deleterious synergism of O_3 and SO_2 upon plants has been described in the original criteria document.[108]

Hammer et al.[113] studied student nurses in Los Angeles prospectively using daily symptom diaries during three years of their training (6). Headache, eye discomfort, cough and chest discomfort were found to be related to ambient daily photochemical-oxidant exposure. Dose-response thresholds could be calculated for each symptom in relation to the daily maximum hourly photochemical-oxidant concentration. They were as follows: Headache - 100 $\mu g/m^3$, eye discomfort - 300 $\mu g/m^3$, cough - 510 $\mu g/m^3$, chest discomfort - 580 $\mu g/m^3$.

The threshold for eye discomfort was comparable to that observed in several earlier experimental and panel studies. Thresholds for cough and chest discomfort were in the same range found in two studies of occupationally exposed workers.[114,115]

On highest oxidant days (800-1000 $\mu g/m^3$), students reported 48% more cough and 100% more chest discomfort than on days when ambient oxidant levels were at or below the present U.S. National Primary Standard (160 $\mu g/m^3$).

Two recent reports summarize new studies on experimental ozone exposure. Kerr et al.[116] studied 20 lightly-exercising subjects exposed to 0.5 ppm ozone for six hours. Symptoms most commonly noted were dry cough and chest discomfort. These symptoms were experienced more frequently by nonsmokers. Significant changes in specific airway conductance (S Gaw), pulmonary resistance (R_L), FVC and FEV_3, but not diffusing capacity (DLCO), were also found. In addition, nonsmokers showed a significant decrease in dynamic compliance during exposure. In general, there was a relationship between experiencing symptoms and alterations in pulmonary function among the study subjects.

Hackney[117] exposed adult male volunteers doing intermittent light exercise to 0.37 or 0.50 ppm of ozone for two hours. These subjects not only developed measurable physiological and biochemical changes, but felt physically ill and were unable to do their normal jobs during exposure and for several hours afterward. All subjects experienced biochemical changes. The least sensitive subjects experienced no respiratory symptoms or physiological changes after five-hour exposures to 0.5 ppm ozone on two successive days. The most sensitive subjects experienced respiratory symptoms after a single two-hour exposure to 0.37 ppm of ozone. The more reactive subjects were generally had a history of asthma, allergy or previous adverse symptom reactions to smog exposure.

No additional effects were observed when 0.30 ppm nitrogen dioxide was added to ozone or after adding 30 ppm of carbon monoxide to O_3-NO_2 mixture. There were no significant changes among the most sensitive subjects during ozone exposures of 0.25 ppm for two hours suggesting that this concentration was a lower limit for these effects in healthy adults.

Three comments about the new evidence are pertinent. First, experimental, occupational and epidemiologic studies of healthy males and females exposed to ozone per se or ambient photochemical oxidants indicates that as little as one to two hours of exposure to 500-600 $\mu g/m^3$ of ozone or photochemical oxidants causes cough, chest discomfort, substernal soreness and impaired pulmonary function in these people. Hence, it would seem that these thresholds should generally hold true for healthy adults and would probably represent an upper limit for especially sensitive persons, e.g., those with asthma or pre-existing cardiovascular disease.

Second, the synergistic effect of ozone and sulfur dioxide on human pulmonary function has been reported in the past two years. This synergism has been described in plants for several years and was summarized in the original criteria document. Also, there is concern that interaction of these two pollutants on lung function may actually be additive and not synergistic. Since lung function is impaired in a non-linear fashion to any stimulus, "extra" decrement attributed to the combination of SO_2 and ozone could be an additive effect in the non-linear part of the lung-function curve.

Third, the terms "radiomimetic" and "mutagenic" should be used with considerable caution when applied to ozone. Animals that showed alterations in red blood-cell fragility had been exposed to 10,000 rads (a large radiation dose) as well as ozone. Chromosomal breaks in peripheral lymphocytes of hamsters following ozone exposure have been observed. But this may just be a peripheral and not a stem cell effect. If so, it is not properly described as a mutagenic effect.

Photochemical oxidants, ozone in particular, are primary irritants aggravating asthma, impairing athletic performance, causing severe respiratory tract irritation and altering pulmonary function in healthy adults under experimental, occupational and ambient exposure conditions. In animals, ozone alters host defenses against infection, causes various structural changes to lung and hematopoietic tissue and produces chromosome breaks in peripheral lymphocytes even at ambient concentrations.

Old and new evidence to date suggests that the present primary National Air Quality Standard for photochemical oxidants of 160 $\mu g/m^3$ (9.08 ppm) maximum concentration for one hour is reasonable. The evidence does not warrant a different standard.

Air quality standards should be based on complete and reliable dose-response relationships. Most quantitative health intelligence to date was obtained from animal models. Direct extrapolation of this research to humans is questionable. Until comprehensive data are accumulated about acute and chronic human exposures, margins of safety will remain obscure.

Exposures of other vulnerable people such as infants, pregnant women and persons with heart and lung disease, have not been investigated. These persons may require more stringent air pollution controls than healthy young adults.

Finally, photochemical oxidants occur with other atmospheric pollutants. Nearly all epidemiologic findings to date may reflect interactions between oxidants and other environmental factors such as ionizing radiation, sulfur oxides or nitrogen oxides. These interactions remain to be discovered in the laboratory and field. Because interactions have not been characterized in laboratory or epidemiologic studies, existing evidence can be applied only with reservations to community exposures.

Considerable human dose-response data under controlled laboratory conditions and in natural community settings are urgently needed to establish protective air quality standards for photochemical oxidants with adequate but no excessive margins of safety.

5.1.5.1 Animal studies--There is much documentation about exposure to ozone at concentrations ≤ 1.0 ppm causing many physiological, biochemical and pathologic conditions in experimental animals. (See Tables 5.11-18.) When the ozone standard was set, extensive data on health effects of ozone were reviewed and summarized in Air Quality Criteria for Oxidants.[109] The purpose of the following review was to bring this document and another[113] up to date and to evaluate significant new information available in the open literature that may have influence on the present standard. Some of the material presented is based on abstracts.

This review is divided into seven sections and limited to those studies where ozone exposure levels were equal to or less than 1 ppm. They include pathology, behavior, infectivity, tolerance, biochemistry, pulmonary function, extra-pulmonary and smog effects. Results are summarized in Tables 11 through 18.

New research is presented in detail elsewhere in this paper. But some of the information can be summarized here. Pulmonary pathology from ozone has been discussed in prior documents.[109,118] The only new information comes from long-term exposure of rabbits to 785.2 $\mu g/m^3$ (.4 ppm) that caused emphysematous and vascular-type lung lesions.[119]

Other researchers found that short-term treatment concentrations as low as 785.2 $\mu g/m^3$ (.4 ppm) reduced bactericidal activity of the lung.[120,121] The primary defensive cell of the lower lung (alveolar macrophage) was also deleteriously affected by low level O_3 exposures [981.5 $\mu g/m^3$ (.5 ppm)].[122-124]

Ozone-induced tolerance to pulmonary edema is a well-recognized phenomenon.[109-118] However, new investigations indicate that short-term exposures to 1963 $\mu g/m^3$ (1.0 ppm) O_3 produced some tolerance to X-irradiation[125] and allergic responses.[126] Several bronchemical changes are also produced by ozone. Many experiments confirmed the anti-oxidant character of Vitamin E that protected animals from some of the harmful alterations produced by ozone.[127-131] This oxidant causes alterations in lecithin information[131-133] and in activities of several pulmonary and serum enzymes.[134-143] Short-term low level O_3 exposures also produced changes in pulmonary function.[128,144,145]

Some interesting systemic O_3 effects are also known. It is possible that this oxidant produced pulmonary artery hypertension in animals that were genetically susceptible.[146] The parathyroid gland was also affected by exposure to 1472.3 $\mu g/m^3$ (.75 ppm) O_3.[3] Additionally, mice that received pentobarbital after exposures of 1963 $\mu g/m^3$ (1 ppm) for three hours/day for three days showed an increased sleeping time. All of the foregoing information is summarized in detail in charts following this section.

While reviewing the O_3 literature, several gaps are noticeable. Most research used healthy, young-adult animals. Attempts were then made to extrapolate this data to people. Since many people are very young, elderly or impaired in some way by various debilitating illnesses, more research should be done with specialized animal models capable of representing these groups.

Also, exposures to O_3 are usually of a long-term intermittent nature suggesting the need for longer-term experiments. Some more recent work also examines the question: Are some pollutant effects naturally reversible? Perhaps more research should attempt to answer this important question. Also, since O_3 induces tolerance to pulmonary edema, it would be worthwhile to examine this matter further.

Some researchers have tried to delineate the actual mechanism of action of O_3, but much work still needs to be done. Furthermore, since most research concentrates on O_3-induced pulmonary damage, it would be of great interest to examine extra-pulmonary effects. The existing data on ozone's systemic effects justify further delving.

5.1.5.1.1 Pathological effects--The pathological effects of O_3 on pulmonary tissue are well documented[109,118] and additional study would only be of interest. Pan et al.[119] exposed rabbits to 785.2 $\mu g/m^3$ (.4 ppm) O_3 for six hours/day, five days/week for 10 months. The authors observed emphysematous and vascular lesions in the lung. The small pulmonary arteries were thicker than controls because of the increased size of the tunica media vasorum that in turn appeared to be a result of tissue edema or muscular hyperplasia in some instances.

5.1.5.1.2 Infectivity--Experiments reported in the initial criteria document[109] showed that three hours of 1570.4 $\mu g/m^3$ (.08 ppm) O_3 enhanced mouse mortality because of subsequent exposures to Group C *Streptococcus pyogenes*. Goldstein et al.[147,148] exposed mice to an aerosol of P^{32} labeled *Staphylococcus aureus* either after 17 hours of O_3 or before four hours of O_3. The concentrations used were 1177.8, 1374.1, 1570.4, 1963 or higher $\mu g/m^3$ (.6, .7, .8 or 1 ppm).

Mechanical clearance and bactericidal capabilities of the lung were then measured. Pollutant exposure for 17 hours before infection caused a decrease in tidal volume and a subsequent decrease in pulmonary deposition of bacteria (67% at 1963 µg/m^3). There were also significant decreases in bactericidal activities beginning at 1963 µg/m^3 (1 ppm).

When the mice were exposed to four hours of O_3 after being infected, slightly different effects were noted. Bactericidal activity was decreased at a lower level--1177.8 µg/m^3 (.6 ppm) and there was no effect on pulmonary deposition or clearance of the Staphylococci. The proposition was advanced that since mucociliary clearance is unaffected by subsequent O_3 exposure, bactericidal defects must be due to dysfunction of another line of pulmonary defense, most probably the alveolar macrophage.

Others working in the same field found that 981.5 µg/m^3 (.5 ppm) of O_3, 16 hours/day for seven months had no effect on the mechanical clearance of polystyrene and iron particles in rabbits. There was only a small decrease in bacterial clearance in guinea pigs.[149]

In other studies,[121] mice were exposed to either 1963 µg/m^3 (.1 ppm) O_3 and 3762 µg/m^3 (2 ppm) NO_2 or 785.2 µg/m^3 (.4 ppm) O_3 and 13731 µg/m^3 (7.27 ppm) NO_2 for 17 hours before infection or four hours after infection. The lung was capable of functioning until the higher pollutant level was reached. Physical clearance was not affected at either level. The injuries demonstrated were those that would be expected from each individual oxidant, so no synergism was noted.

In most of the foregoing studies, the authors recognized the possibility that damage to the alveolar macrophage was primarily responsible for enhanced infectivity and lowered bactericidal response. This functional damage to the macrophage could occur through various mechanisms. First, when rabbits are exposed to 981.5 $\mu g/m^3$ (.5 ppm) for eight hours/day for seven days, they exhibit increased membrane fragility, even though lipid peroxidation was undetectable at this level.[122] Since phagocytosis begins with particle attachment to the cell membrane, this fragility could be involved.

In normal animals, alveolar macrophages are a renewable population, so studies were conducted to see if this process continues after a six-hour exposure to 981.5 $\mu g/m^3$ (.5 ppm), 2159.3 $\mu g/m^3$ (1.2 ppm) and higher levels of O_3. Aging mice (18-20 month-old males) were given injections of tritiated thymidine to mark alveolar cells undergoing DNA synthesis. Inhibi-ion of DNA synthesis occurred at all O_3 levels about equally, representing miximum inhibition. This depression was visible up to 24 hours after ozone mice were transferred to clean air. DNA synthesis did not completely return to normal until 72 hours later.[124]

In a recent study, Fairchild[150] reported on the respiratory deposition of vesicular stomatitis virus in mice after exposure to 1766 $\mu g/m^3$ (.9 ppm) O_3. This exposure produced a 70% increase in respiratory viral deposition. The increase was also due to increased deposition in the nasal cavity. No changes occurred in the lung or trachea. This effect was particularly important since the respiratory volume in O_3-exposed mice was approximately 20% less than in controls. The author suggested that O_3 may increase the severity of infections caused by organisms that primarily exert their effect on or through the nasal mucosa.

5.1.5.1.3 Ozone induced tolerance--Ozone induced tolerance to pulmonary edema has been reviewed in prior documents.[109,118] However, other types of tolerance have been recently investigated. It is interesting to note that when mice were exposed to 1963 $\mu g/m^3$ (1 ppm) O_3 for one hour and then X-irradiated to 800R after 10 days, 60% of these pre-exposed animals survived even though all non-ozonized mice died. This tolerance lasted at least 30 days.[125]

Matsumura[126] investigated the effects of oxidants on induced allergic respiratory disease in guinea pigs. When the animals received a one-hour pretreatment of 1963 $\mu g/m^3$ (1 ppm) O_3, no allergic responses to inhaled acetylcholine were visible after a later exposure to 3926 $\mu g/m^3$ (2 ppm) O_3.

The mechanism of tolerance development to O_3-induced edema is not well understood, but the thymus appears to be involved. Male mice, thymetomized at birth, were unable to develop tolerance to a two-hour dose of 39260 $\mu g/m^3$ (20 ppm) O_3 even though they had been pre-exposed to 588.9 $\mu g/m^3$ (.3 ppm) of O_3 for one hour. Sham-operated animals exhibited tolerance under the same oxidant conditions.[148]

5.1.5.1.4 Pulmonary function effects--Ozone-induced changes have been the subject of many recent reports.

Moorman et al.[128] investigated ozone decomposition in the nasopharynx of beagles by exposing the animals to the gas and measuring mean tracheal concentrations of ozone. One group was chronically exposed to 1963 $\mu g/m^3$ (1 ppm) for three hours/day for 18 months. Another group received an acute one-hour exposure to the same gas concentration. The chronically treated dogs had higher tracheal levels of O_3 due probably to a reduced ability of the upper respiratory system to remove the pollutant.

In another investigation,[144] the right lung of rabbits was exposed to 1963 $\mu g/m^3$ (1 ppm) O_3 for three hours. The left pneumatotic lung was used as a control after the air pressure was returned to normal. The exposed lungs of rabbits sacrificed one and three days after exposure showed reduced vital capacity. Those studied seven days after exposure had only a slight, non-significant, reduced capacity.

Yokiyama[145] also studied the ventilatory functions of guinea pigs before, during and after a two-hour exposure to 981.5 $\mu g/m^3$ (.5 ppm) O_3. The following results were noted: air current resistance increased, frequency of respiration increased and tidal volumes decreased. Comparison studies were made with SO_2 and NO_2 and differences were found. SO_2 produced a decrease in respiratory rates, while NO_2 and O_3 had the opposite effect.

5.1.5.1.5 Extra-pulmonary effects--Most O_3 studies have involved pulmonary effects. But some interesting investigations have shown that O_3 can effect other organs and physiological functions as well. Gardner et al.[152] exposed mice to 1963 $\mu g/m^3$ (1 ppm) O_3 for three hours up to seven days and injected pento-arbital sodium immediately after exposure. There was a significant increase in the sleeping time of the exposed animals after two and three days of O_3 exposure. After one day and after four or more successive exposures, there was no effect. Possibly, this resulted from development of tolerance.

The authors hypothesize that increases in sleeping time might result from formation of ozone reaction-products that could damage hepatic microsomal enzymes that detoxify pentobarbital. The "tolerance" could result from an increase in induction of these enzymes. The actual mechanism of O_3 action is now under investigation.

Circulating blood is also affected by ozone exposure. Female mice inhaled 1688.2 $\mu g/m^3$ (.86 ppm) for eight hours/day, five days/week for six months. At this time, the animals were infected with Plasmodium berghei and exposed mice exhibited increased parasite infestation and increased mortality. Additionally, up to the sixth week of exposure, there was a significant increment in acid resistance of the erythrocytes.[153] Other investigators showed an increased resistance to hemolysis in erythrocytes in mice exposed to 1963 $\mu g/m^3$ (1 ppm) for 30 minutes.[154]

The effects of O_3 on pulmonary arterial pressure was investigated in dogs.[146] Eight animals were exposed to 1963 $\mu g/m^3$ (1 ppm) for 17 months and for varying hours per day. Three dogs developed pulmonary artery hypertension and nine dogs developed excessive systolic pressure. Since there was no proportional relationship between pulmonary artery hypertension and oxidant exposure, it was suggested that the results seen were caused by genetic susceptability.

Matsumura[155] exposed albumin sensitized guinea pigs to 1963 $\mu g/m^3$ (1 ppm) O_3 and found no increases in anaphylactic attacks after subsequent antigen inhalation.

Roth[156] exposed rats to 490.8 $\mu g/m^3$ (.25 ppm) O_3 for two hours and found no differences in gastric secreto-motor activities, even though a temporary effect was present at higher levels.

Atwall,[157] using light and electron microscopy, found histological and ultrastructural changes after a four-eight-hour dose of 1472.3 $\mu g/m^3$

(.75 ppm) O_3 in the parathyroid glands of rabbits. The major changes found in exposed animals were: large number of secretion granules, hyperplasia of chief cells, proliferation and hypertrophy of the rough endoplasmic reticulum, free ribosomes and mitochondria, lipid bodies and an accumulation of secretion granules inside the vascular endothelium of the blood stream.

This increased activity does not abate until 66 hours after exposure. The damage could produce alteration of parathormone production and storage.

Certain radiomimetic properties have already been documented for O_3 and further studies have been made. A review article by Veninga[143] presents evidence for the radiomimetic properties of O_3 and includes some of his own research in the presentation.

C. Black Mice were treated with 392.6 $\mu g/m^3$ (.2 ppm) O_3 for seven hours/day, five days/week during gestation and then for the first 13 weeks of life. 0.9% of the normal newborn mice had unlimited incisor growth while O_3 exposed animals had an incidence of 5.4%. In the same species, neo-natal death rose from 9% to 34% after treatment. Additionally, blepharophimosis in the normal mice occurred in .6% of the animals while it was 9.6% in ozone groups.

Similar, but less dramatic, results were seen in another species of mouse where the rate of blepharophimosis rose from 4.5% to 9.2%. In another study by the same researcher,[142] binucleated lymphocytes in murine blood doubled in number after exposure to 392.6 $\mu g/m^3$ (.2 ppm) for two hours.

5.1.5.1.6 Smog--In the environment, O_3 co-exists with many other pollutants that can modify the actual O_3 effect. Some well-defined studies on pollutant combinations have been reported elsewhere in this manuscript. This section will deal with the effect of synthetic and actual smog on animals.

Emik[123] exposed various laboratory animals to ambient California air over 2.5 years. The average ambient concentrations were .057 ppm oxidant, 1.7 ppm CO, 2.4 ppm hydrocarbons (as carbon), .019 ppm NO_2, .015 ppm NO and 4.2 ppb PAN. The following results were obtained: reduced pulmonary alkaline phosphatase in rats, reduced serum glutamic oxaloacetic transasminase in rabbits, increased pneumonitis in mice, increased mortality in male mice, reduced body weights in mice and decreased running activity of male mice. When older guinea pigs that lived in smog for two years were exposed to 981.5 $\mu g/m^3$ (.5 ppm) O_3 for 10 minutes, they had lowered deleterious responses to O_3 compared to animals that existed in clean air prior to the same O_3 exposure. The authors suggest that a possible adaption occurred. Pulmonary tumors were found in the lungs of some mice, but there was no significan induction of lung adenomas in the two strains of mice exposed to ambient, smog-containing air. And it was thought that this exposure was probably near the threshold of effect.

In further attempts to produce synthetic atmospheres, Nettesheim et al.[158] exposed mice to ozonized, un-leaded gasoline. The maximum concentrations delivered to the animals were 1963 $\mu g/m^3$ (1 ppm) O_3 and 24-30 ppm gasoline for 5.5 hours/day, five days/week for 127 weeks. Some groups of animals were also treated with X-radiation (100R) and infected with influenza virus. Several results were found: irradiation raised the occurrence of lung tumors in females, but not in males;

chronic ozonized gasoline exposure increased the lung tumor incidence in both sexes ($p<.05$) and the viral infection appeared to retard lung tumor growth. The only lung tumors found were adenomas and adenocarcinomas. Furthermore, the investigators state that these experimental conditions had no significant additive or potentiating effects.

Schlipkoeter et al.[159] also investigated the possibility of synergism using a variety of pollutant exposures to mice and rats. They found that 1688.4 $\mu g/m^3$ (.86 ppm) O_3 and (50 and 100 ppm) CO had antagonistic effects on erythrograms.

5.1.5.1.7 Biochemical Effects--The actual toxicity of ozone at the subcellular level is still debatable. However, several theses have been advanced about the biochemical damage caused by O_3. They include the following: (1) non-specific stress with the release of histamine, (2) oxidation of sulfhydryl groups or their precursors, (3) oxidation of polyunsaturated lipids contained mainly in cell membranes, (4) formation of toxic compounds (ozonides) through reaction with polyunsaturated lipid, (5) formation of free radicals, (6) injury mediated by a pharmacologic action, i.e., via a neurohormonal mechanism. These mechanisms have been discussed in the prior document.[109,118] Only new or substantiating material will be presented here.

Many experiments have been conducted to find the effect of O_3 on lipid perioxidation. Chow et al.[136] exposed rats to 1472.3 $\mu g/m^3$ (.75 ppm) O_3 and found an initial decrease and subsequent increase in the activities of glutathione peroxidase, GSH reductase, G-6-PD, 6-P-GD and pyruvate kinase. They reasoned that this pattern was probably due to increased needs for reductive detoxification of lipid peroxide.

Cortes[160] prepared a methyl linoleate ozonide and gave it to rats by IV injection or oral dosage. This treatment was lethal because of acute lung congestion from edema. Significant changes also occurred in the fatty-acid composition of serum and lung lipids. Other experiments where rabbits were exposed to 1963 $\mu g/m^3$ (1 ppm) O_3 for four hours showed a decrease in the rabbits of incorporation of fatty-acids into lecithin. Pulmonary lavage from thse animals indicated increased activity of lecithins.

The authors observed that O_3 may affect the lung by decreasing lecithin formation while simultaneously stimulating the release of surfactant lecthins. Since surfactant serves to protect the host, this lipid damage could have harmful consequences.[132] The formation of pulmonary phospholipid was investigated in another series of experiments. When rabbits inhaled 981.5 and 1963 $\mu g/m^3$ (.5 and 1 ppm) O_3 for one-two weeks, the amount of C^{14} taken into sphingomyelin, lecithin, phospatidyl pthanolamine was significantly reduced. The same researchers further studied these phenomena.[133] Under exposure to 981.5 $\mu g/m^3$ (.5 ppm) O_3, rabbit lungs showed decreased incorporation of C^{14} into lecithin until three hours after exposure when this parameter returned to normal. The reduction in phospholipid formation was more pronounced at two than one week exposure.

That lipid oxidation is a significant cause of toxicity is further supported by many experiments into the role of Vitamin E, an antioxidant. Roehm et al.[129] exposed rats to 1963 $\mu g/m^3$ (1 ppm) O_3 and this resulted in 100% mortality because of pulmonary edema. Fifty percent of the alpha-tocopherol depleted group died in 8.2 days while the vitaminsupplemented rats did not reach a 50% lethal time for 18.5 days. Concurrent studies were carried out with 18810 $\mu g/m^3$ (10 ppm) NO_2 for four weeks and comparisons indicated that O_3 was more toxic and less sensitive to protection by antioxidants. Later investigations by the same group[130] revealed that rats continuously exposed to 1963 $\mu g/m^3$ (1 ppm) O_3 for nine days show a significantly shorter 50% lethal time and greater symptoms of respiratory distress when they were Vitamin E depleted.

When exposure was lowered to 981.5 $\mu g/m^3$ (.5 ppm), pulmonary edema and higher mortalities were noted after six weeks in animals with diets depleted in alpha-tocopherol. The lung weights of the alpha-tocopherol starved rats were also different from those of the diet-supplemented groups. After six weeks of O_3 treatment, significant changes were seen in the fatty-acid compositions of total lung lipid. The most extensive change was an increase in arachidonic acid in both diet groups. But the increase was higher in Vitamin E depleted rats. This effect did not occur until late in the exposure when it was associated with the onset of pulmonary edema and death.

Unlike lung-tissue lipids previously described, fatty acids from endobrochial saline lavage were affected little by O_3 or Vitamin E. In both exposures, the onset of edema was associated with elevated levels of arachidonic acid and another fatty acid (22:6). These two compounds are important constituents of cell membranes, so that could be the site of ozone damage.

A review by Shakman[162] seems to support the idea that ozonolysis causes peroxidation of unsaturated fatty acids of the cell membrane. Additional data[128] from the same group indicated that increases in arachidonic acid and decreases in oleic and linoleic acid after 65 days of 981.5 $\mu g/m^3$ (.5 ppm) O_3 exposure may be responses of the lung to oxidant stress because there was also a depression of serum-reduced glutathione and tissue sulfhydryl compound contents. However, the changed lipid levels could also reflect other metabolic roles of Vitamin E in the bio-synthesis of polyunsaturated fatty acids.

These authors also found concomminent depletion of Vitamin E from erythrocytes of O_3 exposed rats in 23 days vs. 36 days for clean air animals. When others[127] studied the continuous effects on rats of O_3 from 1570.4 $\mu g/m^3$ (.8 ppm) to higher concentrations for seven days, they too found that alpha-tocopheral protected the animals from severe toxicity (mortality) and weight change. At low levels, Vitamin E protection against lung peroxidation was a reciprocal function of the logarithm of dietary alpha-tocopheral.

In a review, Shakman[131] also considered the protective anti-oxidant character of Vitamin E. Since varying dietary conditions exist in the population, perhaps some malnutrition states would represent an impaired group in terms of ozone exposure.

Ozone may affect not only the cell-membrance unsaturated fatty-acids, but may damage acetycholinesterase (ACHE), an enzyme bound to the cell membrane. This was demonstrated in vitro[141] by obtaining ACHE from bovine erythrocytes and exposing it to various concentrations of O_3. The threshold level was 588.9 $\mu g/m^3$ (.3 ppm). Above this level, the enzymatic activity was inhibited.

A whole variety of enzyme activities have been investigated after O_3 exposure. Rats exposed to 1570.4 $\mu g/m^3$ (.8 ppm) O_3 for seven days exhibited increased activities of the pentose shunt and glycolytic enzymes of the lungs.[136]

Murine blood and organs were assayed after exposure to 392.6 $\mu g/m^3$ (.2 ppm) O_3 for periods up to eight hours/day, five days/week for three weeks. The following changes were noted: increase in serum glutamic pyruvic transaminase (SGPT) after two hours of treatment indicating more fat deposits in the liver and increase in hepatic ascorbic acid. There was no change in blood catalase, a strong reducing agent.[142]

A slow, but steady rise in serum protein esterase was also found after rabbits were exposed to 785.2 $\mu g/m^3$ (.4 ppm) for six hours/day, five days/week for 10 months.[135] For 10 months, rabbits inhaled 785.2 $\mu g/m^3$ (.4 ppm) O_3 and concentration of serum trypsin protein esterase trippled by the end of treatment. This rise may reflect thickening of small pulmonary arteries that were also seen.[140]

Mustafa et al.[139] studied mitochondrial oxygen consumption in rats exposed to 1570.4 $\mu g/m^3$ (.8 ppm) for 10-20 days. A 45% increase in lung cellular oxygen utilization was found by the 20th day of the experiment. There was also a 20-30% increase in the oxidation of 2-oxyglutarate and glycerol-1-phosphate. And there was a simultaneous increase (3 fold) in the number of Type II alveolar cells that are rich in mitochondria, suggesting the possibility that increase in O_2 consumption was produced by proliferation of these cells. At 392.6 $\mu g/m^3$ (.2 ppm) O_3 for seven days, there was a 17% increase in oxygen consumption.

Veninga's[143] work, where rabbits were exposed for 60 minutes to 392.6 $\mu g/m^3$ (.2 ppm), showed a small but significant drop in total blood serotonin immediately after termination of O_3. This reduction was probably due to a loss of platelet-bound amine since there was no measurable free circulation plasma serotonin.

In still another study, rats were continuously exposed to 1374.1 $\mu g/m^3$ (.7 ppm) O_3 for five days or 1570.4 $\mu g/m^3$ (.8 ppm) for seven days. The activities of various lysosomal hydrolases were measured in whole-lung homogenates and found to increase significantly. That was attributed to an infiltration of phagocytic cells into the lung in response to O_3. The higher enzymatic levels may also reflect greater cell-membrane lability. And the increase in protease and peptidase activities could be related to chronic obstructive pulmonary disease.[129]

Damage to lysosomal membranes was also suggested by others after histo and cytochemical studies into effects of 1374.1-1570.4 $\mu g/m^3$ (.7-.8 ppm) O_3 continuously for seven days.[134] These researchers saw increased acid phosphatase activity with no change in B-glucuronidase reactivity in alveolar macrophages of rats. The terminal-airway epithlium and adjacent structures also showed increased acid phosphatase activity. This particular enzyme had a nonvacuolar and an intracellular distribution, indicating lysosomal membrane damage.

In another publication, the same authors[135] reported on an examination of similarily exposed rats for enzyme reactivities. In areas of bronchiolar epithelium infiltrated by mononuclear cells, there was a lower NADH- and NADPH- diaphorase activity and increased ATPase activity. However, intra-alveolar septa in the centriacinar region had increased diaphorase, LDH, ATPase and cytochrome oxidase activities. These increases were also seen in septa that were not thickened or infiltrated with increased numbers of cells. It is suggested that these enzymatic changes are parts of protective-adaptive mechanisms that operate mainly in the centriacinar region of lungs.

Trams et al.[163] found no lipid peroxidation in brain tissue of dogs chronically exposed to 1963 $\mu g/m^3$ (1 ppm) O_3.

5.1.5.1.8 Behavior Effects--Several studies have shown the effect of ozone on behavior patterns in animals. When rats were intermittently exposed to O_3 between 588.9-981.5 $\mu g/m^3$ (.3-.5 ppm) and clean air over a two-month period, they required a longer time to learn specific tasks and their learning was quite unstable compared to controls. And they exhibited reduced ability to discriminate temporal events such as judging lengths of time.[164]

Xintaris et al.[165] studied the evoked response to flash in the specific visual cortex and in the superior colliculus of rats in response to exposures of 981.5-1963 $\mu g/m^3$ (.5-1 ppm) O_3 for one hour and found depression of responses. He suggested that altered evoked responses reflect possible morphological or functional change in the central nervous system. Other researchers[166] exposed rats to 98.11, 196.3, 392.6, 981.5 and 1963 $\mu g/m^3$ (.05, .1, .2, .5 and 1 ppm) O_3 and found that the greater the concentration of gas, the greater the depression in gross motor activity.

The pollutant-exposed animals also had prolonged periods of inactivity and an increase in urination rates. In another series of experiments,[167] sub-human primates showed an elevation of both simple and choice reaction time in atmospheres of 981.5 $\mu g/m^3$ (.5 ppm) O_3 after only a 30-minute pre-exposure to this concentration. When Fletcher[127] continuously exposed rats to 1963 $\mu g/m^3$ (1 ppm) for seven days to O_3, he found an 84% reduction in voluntary activity.

Table 5.16. PATHOLOGICAL CHANGES CAUSED BY OZONE

O_3 μg/m^3	O_3 ppm	Length of Exposure	Observed Effect(s)	Species	Ref
785.2	.4	6 hrs/day 5 days/wk 10 mos.	Emphysematous and vascular-type lesions were observed in lungs and small pulmonary arteries were thicker.	rabbits	116

Table 5.17. EFFECTS OF OZONE ON INFECTIVITY

O_3 µg/m^3	O_3 ppm	Length of Exposure	Observed Effect(s)	Species	Ref
1963	1	17 hrs. prior to bacteria	Decrease in bacterial pulmonary deposition (67%) decrease in bactericidal activity.	mice	144
1177.8	.6	4 hrs. after bacteria	No effect-bacterial deposition clearance. Bactericidal activity decreased.	mice	144,145
981.5	.5	16 hrs/day 7 mos.	No effect-mechanical clearance of polystyrene and iron particles.	rabbits	146
981.5	.5	6 hrs.	Lowered rates of DNA synthesis in alveolar cells.	aging mice	121
981.5	.5	8 hrs. x 7 days	Increased fragility of alveolar macrophage.	rabbit	119
785.2	.4	4 hrs.	Bactericidal activity inhibited by O_3, but an induced silicotic condition played no role.	mice	117
785.2	.4	17 hrs. prior to bacteria or 4 hrs. after	Mice also exposed to 7.27 ppm NO_2 simultaneously. Physical clearance not affected, but bactericidal activity was. No synergism noted.	mice	118

Table 5.18. OZONE INDUCED TOLERANCE

$\mu g/m^3$ Pre-Exposure	O_3 ppm Pre-Exposure	Length of Pre-Exposure	O_3 $\mu g/m^3$ after Latent Period	O_3 ppm after Latent Period	Length of Exposure after Latent Period	Observed Effect(s)	Species	Ref
188.9	.3	1 hr.	39260	22	2 hrs.	Thymectomized animals do not develop tolerance while sham operated animals do.	mice	148
963	1	1 hr.				All animals X-irradiated to 800 R. 60% of O_3 pre-exposed mice survived. 100% of controls died.	mice	122
963	1	1 hr.	3926	2	1 hr.	Tolerance to allergic response to inhaled acethylcholine.	guinea pigs	123

Table 5.19. EXTRA-PULMONARY EFFECTS OF OZONE

O_3 μg/m^3	O_3 ppm	Length of Exposure	Observed Effect(s)	Species	Ref
1963	1	3 hrs./day, 2 day	Increased sleeping time due to pentobarbital.	mice	149
1963	1	17 mos. various hrs/day	Some animals developed pulmonary artery hypertension, probably because of genetic susceptibility.	dog	143
1963	1	30 mins.	Increased resistance to erythrocyte hemolysis.	mice	151
1963	1		Sensitized animals did not show increases in anaphylaxis after antigen challenges.	guinea pig	152
1688.2	.86	8 hrs/day 5 days/wk. 6 mos.	Increased infestation and mortality after infection with P. berghei. Increased acid resistance of erythrocytes.	mice	150
1472.3	.75	4-8 hrs.	Parathyroid gland examination showed: larger numbers of secretion granules, hyperplasia of chief cells, proliferation and hypertrophy of rough endoplasmic reticulum, free ribosomes and mitochondria lipid bodies, and accumulation of secretion granules inside vascular endothelium. These changes reverted to normal 66 hours after exposure.	rabbit	154
490.8	.25	2 hrs.	No differences in gastric secreto-motor activity.	rat	153
392.6	.2	7 hrs/day 5 days/wk. during gestation and 3 wks. after birth	Unlimited incisor growth was seen in .9% of the normal and 5.4% of the treated mice. Neo-natal death increased from 9% to 34%. Blepharophimosis rose from .6% occurrence to 9.6% in one species and from 4.5% to 9.2% in another species.	mice	140
392.6	.2	2 hrs.	Binucleated lymphocytes in blood doubled in number after exposure.	murine	145

Table 5.20. EFFECTS OF SMOG

O_3 µg/m^3	O_3 ppm	Length of Exposure	Observed Effect(s)	Species	Ref
1963	1	5.5 hrs/day 5 days/wk. 127 wks.	Animals received ozonized gasoline (24.30 ppm gasoline). Some were X-radiated and others infected with influenza. Ozonized gasoline increased lung tumor incidence in both sexes.	mice	155
1688.4	.86		Exposures in combination with 50 and 100 ppm CO produced antagonistic effects on erythrogram.	mice rats	156
ambient smog	(.057 ppm)	continuous 2 yrs.	Exposure to ambient smog consisting of oxidant (.057 ppm), CO, hydrocarbons, NO_2, NO and PAN resulted in reduction in some enzymes in rats and rabbits, increased pneumonitis in in mice, increased mortality in mice, reduced body weights in mice and decreased running activity in mice. Guinea pig showed adaption to later O_3 exposure.	rats rabbits mice guinea pig	120

Table 5.21. EFFECT OF OZONE ON PULMONARY FUNCTION

O_3 μg/m^3	O_3 ppm	Length of Exposure	Observed Effect(s)	Species	Ref
1963	1	8 hrs/day 18 mos.	Chronic exposure resulted in higher tracheal of O_3.	dog	125
1963	1	1 hr.			
1963	1	3 hrs.	1-3 days post exposure had reduced the animals' vital capacity. With seven days post exposure, the netal capacity was reduced only slightly.	rabbit	141
981.5	.5	2 hrs.	O_3 caused an increase in air current resistance and frequency of respiration and a decrease in tidal volume.	guinea pig	142

Table 5.22. BIOCHEMICAL EFFECTS

O_3 μg/m^3	O_3 ppm	Length of Exposure	Observed Effect(s)	Species	Ref
1963 981.5	1 .5	4 hrs. Continuous 1-2 wks.	Decreased licithin formation and release of surfactant lecithins.	rabbit	129, 130, 158
1963 981.5 1570.4	1 .5 .8	Continuous 9 days 7 days	Vitamin E acts as an antioxidant and protects against some O_3 alterations (mortality, high increases in arachidonic acid content and lipid peroxidation).	rats	126,128 125,127 128
1963	1	Chronic	No lipid peroxidation in brain tissue.	dog	160
1570.4	.8	7 days	Increased activities of pentose shunt and glycolytic enzymes of lungs.	rats	133
1570.4 392.6	.8 .2	10-20 days	At the higher concentration: increase in the lung mitochondrial O_2 consumption in oxidation of 2-oxyglutarate and glycerol-1-phosphate and the number of type II alveolar cells rich in mitochondria. And at the lower O_3 concentration: increase in O_2 consumption.	rats	136
1374	.7	5 days 7 days	Lysosomal hydrolases in whole-lung homogenates and tissue sections increased. Increase in protease and peptidase were seen along with other enzymatic changes.	rats	131,134
1374.1 7670.4	.7 .8	Continuous 7 days	Bronchiolar epithelium had lower NADH and NADPH diaphorase activity and higher ATPase activity.	rats	132
1472.3	.75		Initial decrease and subsequent increase in activities of glutathione peroxidase, GSH reductase, G-6-PD, G-P-G) and pyruvate kinase.	rats	133

Table 5.22 (continued)

785.2	.4	6 hrs/day 5 days/wk 10 mos.	Use in serum protein esterase.	rabbits	135
785.2	.4	10 mos.	Increase in serum protein esterase.	rabbits	137
588.9	.3		Acetycholinesterase inhibited.	_in vitro_	138
392.6	.2	8 hrs/day 5 days/wk. 3 wks.	Increase in serum glutamic pyruvic transaminase, and hepatic ascorbic acid. No change in blood catalase.	murine	139
392.6	.2	60 mins.	Small decrease in total blood serotonin.	rabbits	140

Table 5.23. BEHAVIORAL EFFECTS

O_3 μg/m^3	O_3 ppm	Length of Exposure	Observed Effect(s)	Species	Ref
1963	1	Continuous	84% reduction in voluntary activity.	Rats	124
588.9	.3	Intermitten	Required a longer time to learn specific tasks.	Rats	159
961.5-1963	.5-1	One hour	Depression of evoked response to flash.	Rats	160
981.5	.5	30 minutes	Elevation of simple and choice reactive time.	Sub-human primates	164
98.11	.05		Depression of gross motor activity. Increase in rate of urination.	Rats	163

5.1.6 Total Suspended Particulates

5.1.6.1 Human Studies--The national primary air-quality standard for total suspended particulates is 75 $\mu g/m^3$ (geometric mean) when measured as an annual average and 260 $\mu g/m^3$ when measured on a daily basis.

5.1.6.1.1 Evidence for the standard--The current national primary air-quality standards for particulate matter are shown in Table 5.24. These standards are based on evidence of adverse health effects ranging from symptoms of increased irritation to excess mortality associated with various concentrations and durations of particulate exposure (Table 5.25). Although it was not possible in these studies to entirely separate effects of particulate and sulfur dioxide, setting separate standards for both was wholly consistent with the Administrator's legislated obligation to provide adequate safety margins in setting ambient air-quality standards.

Although these epidemiologic studies were the best available at the time, their limitations were recognized. Chapter 11 of the Particulate Criteria Document fully and completely discusses interpretative cautions.

In brief, measurement methods were not often directly comparable. The physics of particle size and chemistry of particulate matter had almost always been ignored in field studies and pollution and health indices were not always measured over the same time periods. Few studies identified or adjusted for all other known or possible morbidity determinants such as cigarette smoking, occupational and other past exposures, past medical history, socioeconomic status, residential mobility and indoor pollution exposure.

Table 5.24. U.S. NATIONAL PRIMARY STANDARD FOR TOTAL SUSPENDED PARTICULATES

Pollutant	U.S. National Primary Standard Concentration ($\mu g/m^3$)	Averaging Time
Total Suspended Particulates	75*	Annual geometric mean
	260	24 hours

*Geometric mean

Also, almost no epidemiologic studies had been possible in areas characterized solely by particulate matter. And almost no studies of highly susceptible individuals had been done.

5.1.6.1.2 Interim Evidence--Subsequent evidence on health effects of particulate pollution is summarized in Table 5.26. These studies were also complicated somewhat by presence of considerable amounts of sulfur dioxide. Despite that complication, best judgment estimates for the various health effects that have been associated with particulate exposures are given in Table 5.27.

These data strengthened and extended the initial observations on health effects. The CHESS studies were designed to indentify or adjust for effects of other possible disease determinants in addition to ambient air pollutants. The limitations of the CHESS studies differ for the short-term and long-term health effects studies.

For the studies of short-term health effects, estimates of exposure are more reliable. But the indicators used to measure health effects require further quantitative refinement. For the studies of

Table 5.25. SCIENTIFIC EVIDENCE FOR THE U.S. NATIONAL PRIMARY TOTAL SUSPENDED PARTICULATE STANDARD

Adverse Health Effect	Concentration at which effect was observed		References
	Concentration ($\mu g/m^3$)	Averaging Time	
1. Increased mortality.	750 or a rise of 200	24-48 hours	165,166
2. Increased infant mortality and cancer deaths.	200	2 days	167
3. Increased upper respiratory infection and cardiac morbidity.	375*	24 hours	168,169
4. Excess bronchitis mortality.	200	24 hours	170
5. Acute worsening of symptoms in bronchitis patients.	300	Daily	171
6. Increased mortality from chronic respiratory disease and all causes.	100	2 years	172
7. Increased chronic respiratory disease prevalence in adults; increased upper and lower respiratory tract disease and diminished pulmonary function in children.	100-200	Annual	173,175

*Converted from 3 COH units (let 1 COH = 125 $\mu g/m^3$).

long-term health effects, previous exposures had to be estimated because of incomplete exposure monitoring data. Hence, estimates of exposure were somewhat less accurate. But the observed health effects were quite consistent.

5.1.6.1.3 New Evidence--Few epidemiologic studies on long-term exposure to total suspended particulates have appeared recently. Those that have appeared come from the CHESS program of EPA. Responses related to long-term effects include chronic respiratory disease and lower acute respiratory disease. Recent findings from CHESS relevant to long-term health effects of particulate pollution have come from studies in New York and Birmingham-Charlotte.

Of the two sets of findings, those from Birmingham-Charlotte are more directly relevant to particulate health effects since the SO_2 pollution there is minimal. For that reason, the Birmingham-Charlotte findings will be presented first and in more depth than the New York observations.

- Birmingham-Charlotte Chronic Respiratory Disease

During November, 1971 in Birmingham, Alabama and Charlotte, North Carolina, the rate of chronic respiratory disease symptoms for parents of elementary school children was determined by self-administered questionnaires. Survey results noted small, but not statistically significant differences, in prevalence between the cities. Observed difference included the direction of pollution exposure. Birmingham was higher. The equivocal nature of prevalence difference in this study made it difficult to form firm conclusions about the relationship of air pollution to chronic respiratory disease. It appeared that long-

Table 5.26. SUBSEQUENT SCIENTIFIC EVIDENCE RELATING TO THE U.S. NATIONAL PRIMARY TOTAL SUSPENDED PARTICULATE STANDARD

Adverse Health Effect	Concentration at Which Effect Was Observed		References
	Concentration ($\mu g/m^3$)	Averaging Time	
1. Increased cough, chest discomfort and restricted activity.	100-269	24 hours	176
2. Aggravation of cardio-respiratory symptoms in healthy persons and in elderly patients with heart and lung disease. Increased asthma attacks in people with asthma.	80-100	24 hours	177
3. Aggravation of cardio-respiratory disease symptoms in elderly patients with heart or chronic lung disease.	76-260	24 hours	177
4. Decreased pulmonary function in schoolchildren	110	Annual	178
5. Increased frequency and severity of acute lower respiratory diseas in schoolchildren.	100	Annual	179
6. Increased chronic respiratory disease symptom prevalence in adults.	100	Annual	180

Table 5.27. BEST JUDGMENT THRESHOLD ESTIMATES FOR HEALTH EFFECTS OF TOTAL SUSPENDED PARTICULATES

Adverse Health Effect	Best Judgment Threshold Estimate	
	Concentration (μg/m^3)	Averaging Time
1. Excess mortality.	250-300 100-175	24 hours Annual
2. Aggravation of symptoms in the elderly.	80-100	24 hours
3. Aggravation of chronic lung disease.	>250	24 hours
4. Aggravation of asthma.	100	24 hours
5. Acute irritation symptoms.	170	24 hours
6. Decreased lung function in children.	100	Annual
7. Increased prevalence of chronic bronchitis.	100	Annual
8. Increased acute upper and lower respiratory illness in families and in schoolchildren.	100	Annual

term exposure to total suspended particulates at 150 $\mu g/m^3$ or less in the presence of low sulfur dioxide was not strongly related to chronic respiratory disease symptoms.[184]

- Birmingham-Charlotte Lower Acute Respiratory Disease

The acute lower respiratory disease experience of 10,000 children aged 1-12 years was determined in a retrospective survey of the children's parents. During the 12 years prior to the survey, estimated total suspended particulate exposure ranged from 103 to 168 $\mu g/m^3$ in Birmingham and from 72 to 107 $\mu g/m^3$ in Charlotte while SO_2 was less than 25 $\mu g/m^3$. Significant increases in pneumonia and croup among blacks and "any lower respiratory disease," bronchitis and croup among whites, were noted in Birmingham residents. Since increases were noted in children aged one to four, the authors' best judgment as to the level of total suspended particulate capable of producing an effect is between 103 and 139 $\mu g/m^3$ in the presence of low sulfur dioxide.[185]

- Birmingham-Charlotte Acute Respiratory Disease

Panels of families in both Birmingham and Charlotte sent bi-weekly reports of their morbidity status for 16 week periods in 1970-71 and 1971-72. Incidence of acute respiratory disease did not show a consistent relationship with air pollution, although data on severity of illness among residentially stable families did indicate that exposure to high air pollution was associated with restricted activity and physician visits. Best judgment estimates of air pollution effect are 90 $\mu g/m^3$ TSP, 12 $\mu g/m^3$ SS, and 3 $\mu g/m^3$ SN for three years' exposure.[186]

- New York Studies

Chronic respiratory disease rates among parents of elementary school children was not elevated in areas of higher particulate and sulfur dioxide exposure. Complicating the interpretation of a unique particulate effect was the presence of a previous study that did observe an effect coupled with a long-term decline in levels of both TSP and SO_2 and a short-term dramatic decrease in SO_2 between the two studies.[187] Lower acute respiratory disease was, however, shown to be higher in areas of higher particulate and SO_2 exposure. The authors' best judgment of the exposures associated with increased lower respiratory disease were 175-250 $\mu g/m^3$ SO_2, 85-110 $\mu g/m^3$ TSP and 13-14 $\mu g/m^3$ suspended sulfates.[188]

Similar to the long-term health effect of particulates, few new studies have investigated short-term effect. Studies involving panels of asthmatics, elderly and families have been used to obtain data relating to any short-term effect. Again, studies done in Birmingham and Charlotte are more likely to be relevant to such effects than studies done in New York.

- Birmingham-Charlotte Episodes

Acute irritation symptoms reported by 1500 families of elementary school children were studied in Birmingham, Alabama and Charlotte, North Carolina during 1971 and 1972. Following three designated air pollution episodes (two only for Charlotte) and one control period, telephone interviews were conducted and responses compared across all time periods for each participating family member. Although Birmingham residents did experience an elevated symptom rate in the designated air pollution episodes, especially the first, Charlotte residents did not. The rate of symptoms even in Birmingham did not vary with level of pollution experienced by Birmingham residents across all episodes.[189]

- Birmingham-Charlotte Asthma

Panels of asthmatics located in Birmingham and Charlotte were observed from the fall to the spring of 1971-72. Aggravation of asthmatic attacks was not shown to be related to TSP or RSP. Some relationship with suspended nitrates was noted. No reliable estimate of the level of nitrates necessary to produce an attack could be made because of analytic problems associated with air sampling.[190]

- New York Studies

The New York studies add relatively little information to the short-term TSP exposure data base. Adult panels of well and cardiopulmonary patients show a TSP effect of between 70 and 120 $\mu g/m^3$ 24 hour average. These effects, however, occur in the presence of significant quantities of sulfur dioxide.[191] Studies of asthmatics showed no association with TSP, but did with suspended sulfates and nitrates.[192] The observed threshold levels were 8 $\mu g/m^3$ and 3 $\mu g/m^3$ 24 hour values respectively. However, there is a question about the accuracy of the analytic technique used for suspended nitrates so that the 3 $\mu g/m^3$ level should be considered with caution.

5.1.6.1.4 Discussion--Results from the previously discussed studies have not significantly altered the state of the art knowledge of health effects of total suspended particulates. Results from long-term studies (chronic respiratory disease, lower respiratory disease and acute respiratory disease) were unable, because of their design, to distinguish between total particulates and respirable particulates. Similarly, these studies were not able to explain the possible effect of chemical composition of particulates because of the nature of the study design. The studies, however, did further document health effects associated with long-term exposure of about 100 μg/m^3 (lower respiratory disease and acute respiratory disease).

Short-term health studies were somewhat more effective in providing insight into the relative importance of respirable to total particulates and possible importance of chemical composition. Studies of asthmatics did not show any relationship between asthmatic attacks and either total suspended particulates or respirable particulates, but did with suspended sulfates and suspended nitrates. Aggravation of symptoms in panels of adults was most often associated with suspended nitrates, respirable particulates and total suspended particulates. There was little difference in the strength of the relationship between health effects associated with respirable particulates as compared to total particulates.

Table 5.28 presents the best judgment estimates of effects from particulate exposure based on the new evidence summarized above. In general, few modifications are noted from the estimates presented in Table 5.27 and most modifications are relatively minor. These results seem to indicate that the annual average TSP standard of 75 μg/m^3 (geometric mean) is still quite acceptable, but some modification in the 24-hour standard may need to be considered because of the evidence from the adult panels. Since the question of respirable vs. total and chemical composition of particulate matter has existed for a number of years, definitive studies designed to find the answers to these questions are needed and should be conducted in the near future.

Table 5.28. BEST JUDGMENT THRESHOLD ESTIMATES FOR HEALTH EFFECTS OF TOTAL SUSPENDED PARTICULATES BASED ON NEW EVIDENCE

Adverse Health Effect	Best Judgment Threshold Estimate	
	Concentration ($\mu g/m^3$)	Averaging Time
1. Aggravation of Symptoms in adult panels.	120	24 hours
2. Acute irritation symptoms.	175	24 hours
3. Aggravation of asthma symptoms.	260	24 hours
4. Increased prevalence of chronic bronchitis.	100	Annual
5. Increased lower respiratory disease in schoolchildren.	90	Annual
6. Increased acute respiratory disease.	90	Annual
7. Decreased lung function in schoolchildren.	120	Annual

Table 5.29. ESTIMATED POPULATION AT POTENTIAL RISK TO POLLUTANT-INDUCED EFFECT

Adverse Health Effect	Expected Proportion of the Population at Risk (Rate per 100)	Expected Size* of Population at Risk
1. Mortality.	23+	32,220,000
2. Symptom aggravation in the elderly.	23+	32,220,000
3. Aggravation of chronic lung disease.	20 to 40**	28,000,000 to 56,000,000
4. Aggravation of asthma.	3 to 5**	4,200,000 to 7,000,000
5. Acute irritation symptoms.	100**	140,000,000
6. Decreased lung function in children.	20++	28,000,000
7. Increased prevalence of chronic bronchitis.	100**	84,000,000
8. Increased acute respiratory diseases.	100**	140,000,000

* Assumes 70% of 200,000,000 persons live in U.S. urban areas.
+ Proportion of population aged 50 or more.
**Proportion of population aged 20 or more.
++Proportion of population aged 5 to 14.

5.1.6.2 Toxicology--At this point in time, theoretical definition of suspended fine particles as they relate to health must necessarily be broad and somewhat arbitrary. The deposition of particles anywhere in the respiratory tract, from the nose to the alveoli, may produce significantly harmful effects on health. There is some reason to believe, however, that non-viable particles deposited below the trachea may be more harmful than those deposited in the nasal cavity.

Whether particles must reach the alveoli to harm is a more controversial issue. It is reasonable to assume that particles deposited in the bronchi or bronchioles are more important in producing bronchitis than those deposited in the alveoli. At present, there seems to be little value in confining the category of suspended fine particles only to those particles that reach the alveoli.

The Task Group on Lung Dynamics has calculated that up to 10% of inhaled particles of diameter 2.5 μm are deposited in the tracheobronchial compartment and that up to 30% are deposited in the alveolar compartment. Most particles of diameters above 5 μm are deposited in the nasal cavity. That means a size range of fine particulate up to 205 μm diameter, measured aerodynamically, is of principal interest from the standpoint of health effects.

Toxicological properties of inhaled particles are related to a complex of factors that include specific physical-chemical properties of the particles themselves and host conditions that affect response to exposure to these particles. As for toxicity of certain specific particulates that may exist in the atmosphere, moderate amounts of information are known. But such information is often unavailable in a form suitable for accurate assessment of minimum time-concentration for exposure that will adversely affect health.

Even less information is known about how physical environmental variables (weather conditions) may interact with suspended particulate matter and alter its chemical composition and affect its toxicity. Weather conditions, per se, may affect man in such a way as to alter his exposure to inhaled particulates. The information that is available, however, provides a basis for estimating relative toxicity of certain substances and provides insights into problem areas where our information is inadequate.

5.1.6.2.1 Dose-Response Relationships--The principal way air particulates exert an effect on health is presumed to be through inhalation and consequent effects on the respiratory system. This presumption is acceptable in determination of short-term effects of irritant aerosols. Such an assumption may be less tenable in consideration of long-term exposure effects where such responses as carcinogenesis, mutagenesis and subtle metabolic effects result from whole body burdens. In these cases, other routes of entry besides inhalation may be important in establishing dose-response relationships.

Inhalation, however, may be a significant route of entry for non-respiratory toxicants that are first deposited in the respiratory system, but then translocated to the gastro-intestinal system by mucociliary transport and swallowing. There they may exert a primary toxic effect or be absorbed and translocated to other tissues where an adverse health effect might occur.

5.1.6.2.2 Physical Factors--Most calculated and experimental data on respiratory deposits of particles uses the term "aerodynamic diameter."

Effective aerodynamic diameter is a function of particle size, density and shape. The distribution and mean of aerodynamic diameters are required to predict patterns of deposit in the respiratory tract.

In terms of mass, many aerosols fit a log-normal distribution, that is, the logarithms of particle size are normally distributed. Thus, two indices are used to describe particle distribution: (1) the mass median aerodynamic diameter (MMAD) and the distribution parameter (σg) that represents geometric standard deviation.

The MMAD is the particle size in a log-normal distribution below which 50% of total mass resides. The σg is the ratio of particle sizes at 50.0% and 84.13% probability. These parameters, then, are used to determine the mass of material that may be deposited in a given lung compartment.

In some cases, especially with fine suspended-particle materials, numbers of particles may be more relevant than mass. To relate number of particles to mass size distribution requires determination of frequency distribution. Particle number can be toxicologically important since the large surface area may promote gas-particle interaction or volatile substance-particle interaction. Coupled with small size, these interactions may result in deeper penetration in the respiratory tract and more rapid dissolution. Surface area is also important for highly insoluble particles that show their toxic potential only at the surface.

Another important factor in regional deposition of inhaled particles is hygroscopicity. Particles as usually measured externally are not saturated with water. The growth of sodium chloride particles is a function of relative humidity as demonstrated in an experimental study by McJilton, Frank and Charlson.[194] Particle size increased when relative humidity exceeded 75%. The respiratory tract, with its saturated atmosphere, may increase effective particle size considerably over and above that measured in ambient air. However, hygroscopicity is of less significance with particles of high density.

A moderate amount of information is available on respiratory particle deposition in people and lower animals. These data have been critically reviewed by Morrow[195] and others.[196,197] These data are based on mathmetical calculations and to a limited extent, experimental data obtained from man. The calculated data agree in general with experimental observations of people.

A figure depicting respiratory deposition of particles as a function of particle diameter is shown in Figure 5.4. These data indicate that most particles larger than five μm are deposited in the nasal cavity or nasopharynx. As particle size becomes smaller, an increasing number of particles are deposited in lungs. This is a possible explanation of experimental results by Amdur who reported that sulfate aerosols of 1 μm diameter are greater respiratory irritants for guinea pigs than 2-3 1 μm-sized aerosols.[198-201]

Only a few comparisons to people have been made on regional respiratory particle deposition in laboratory animals. (Figure 5.5)[202-204] Although there have been some differences in particle deposition in rodents, especially in efficiency of nasal deposition, patterns are sufficiently similar to justify use of laboratory animal experimentation in inhalation toxicology.

Each of the shaded areas (envelopes) indicates variability of deposition for a given mass median (aerodynamic) diameter in each compartment when distribution parameter σg varies from 1.2 to 4.5 and tidal volume is 1450 ml.

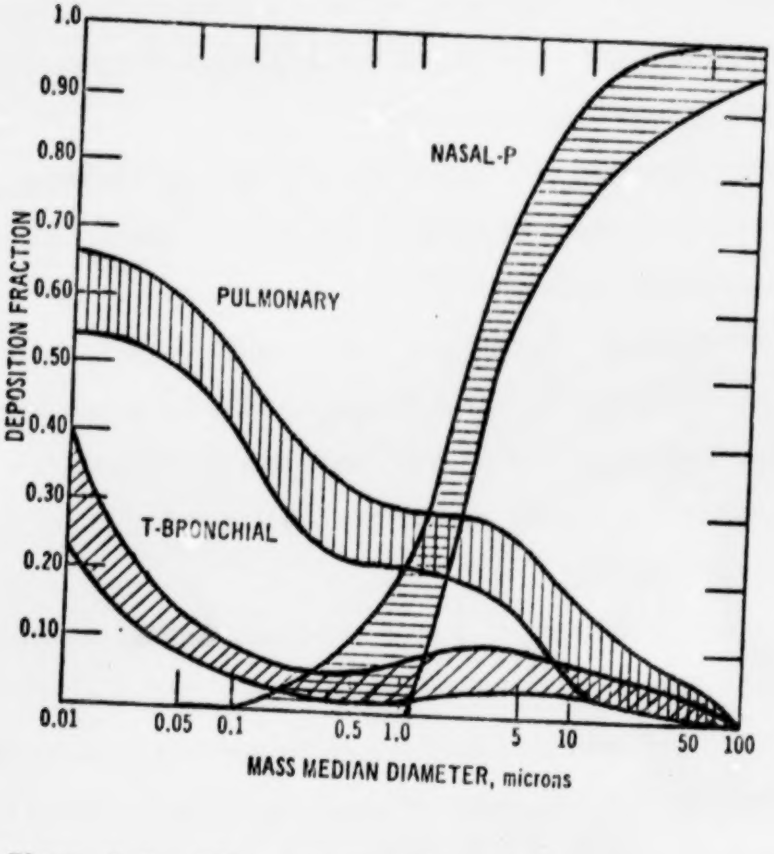


Figure 5.4. Effect of particle size on regional respiratory particle deposition in man

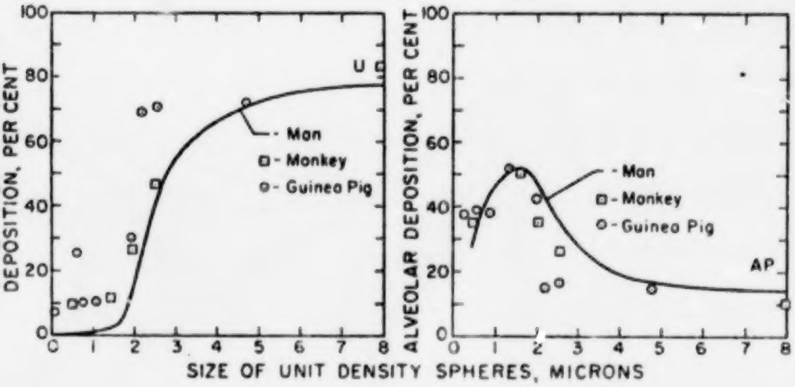


Figure 5.5. Deposition vs. particle size of inhaled particles in the upper respiratory tract and lungs of guinea pigs and monkeys compared to people

A major question exists, however, about applicability of respiratory deposition data from normal individuals to predictions of how exposure to suspended particulate matter may affect particle deposition rates and regional deposition. To the extent that suspended particulates may act as respiratory irritants, consequent effects on mechanics of breathing may affect both the rate and site of particle deposition.[205,206]

Under these circumstances, total inhaled dose may be increased. However, this hypothesis lacks experimental verification. Also, many diseases and symptoms associated with elevated levels of particulate matter are airway related. In these diseases, the contribution of inhaled particulate matter to their pathogenesis may not require penetration into the alveolar region to produce a toxic effect. This point cannot be fully evaluated, however, since pathogenesis of chronic obstructive lung disease is not adequately understood.

Finally, as noted recently by Casarett[207] the varied pulmonary responses to particles can readily be seen as interacting with effects produced by gases. In any case, it is clear that effects of complex mixtures of gases and particles are not likely to be accounted for by simple summation of individual components.

5.1.6.2.3 Host-related Factors--The state of health, especially of the cardiorespiratory system and the amount of activity of an individual affect the total amount and site of deposition of particulates that an individual may inhale at any given time. The pattern of breathing affects the depth of particle deposition, i.e., deep breathing increases alveolar deposition of particles. During exercise, people commonly shift from nose to mouth breathing and probably increase particle penetration into lungs as a result.[201]

At the same time, exercise increases respiratory volume that then increases the inhaled dose of any toxicant. This effect of exercise has been demonstrated in people experimentally exposed to ozone,[208] and would presumably occur with inhalation of particulates as well.

Pre-existing disease of the airways or alveoli is though to predispose affected individuals to more severe response when subsequently exposed to atmospheres that contain high amounts of suspended particulate matter. Exacerbation of symptoms of disease that occur in such individuals usually occur in conjunction with weather conditions, i.e., cold and high relative humidity, that in themselves may have adverse health effects.[209,212] Just how interaction between physical weather factors, particulate matter and gaseous pollutants interact to affect health is not well understood.

5.1.6.2.4 Retention Factors--The deposition rate and retention time of inhaled particles are separate phenomena with overlapping biologic effects. Particle retention time depends on (1) site of initial deposition in the respiratory tract and (2) chemical composition and properties of the particles.

If particles are deposited in ciliated epithelium of airways, particle clearance is reasonably rapid.[213] In this event, the toxicity depends on solubility of the particle in mucus while in transit up the muco-ciliary escalator. If the particle is highly soluble, toxic inflammation in the airway epithelium may occur.

Particles deposited in alveoli of lungs may only very slowly clear from this location.[196,214,216] The extent of clearing reflects solubility and subsequent translocation via lymphatic drainage or macrophage phagocytosis and clearance via muco-ciliary transport mechanisms.[217]

The preponderance of evidence, however, is that non-soluble particles remain in the deep lung for long periods of time (weeks, months and even years). As a result of this slow clearance, carcinogenic hazard of long-lived radioactive metals, i.e., plutonium and uranium and airborne chemicals, especially hydrocarbons, is of special concern.

A recent hypothesis by Kilburn[218] of a two-zone distal lung merits some consideration of deep lung clearance of particles of limited solubility . The first zone consists of cul-de-sac alveolar ducts with "resident" macrophages that assist in enzymatic digestion of particles for clearance only to lymphatics or blood vessels. The second zone is represented by respiratory and terminal bronchioles permeable to macrophages and polymorphonuclear leukocytes. These cells are subject to recruitment when dusts contact "sentinel" macrophages in the area. This hypothesis is consistent with a considerable body of circumstantial evidence and deserves further investigation.

A second hypothesis expressed by Casarett,[207] not exclusive of the one just presented, is that phagocytosis by macrophages or, to a lesser extent, by alveolar epithelial cells, is preliminary to removal of particles whatever their subsequent destination. So Casarett[207] supports a concept of a rate-limiting biological process in lung clearance composed of phagocytosis and cellular movement. This concept does not deny the importance of physicochemical indices,[219] but views them in terms of their influence on interaction between particle and cell.

In support of this view, it can be said that the central role of the alveolar macrophage in defense of the lung against insult by particulate material is now firmly established.[220,221] Investigations to examine influence of particulate materials and soluble analogues on structural and functional integrity of alveolar macrophage have been reported recently by Bingham et al.,[222] Burrell and Anderson[223] and Waters, Gardner and Coffin.[224]

There is much evidence that particles that penetrate into fixed tissues show clearance half-times ranging from a few days to thousands of days. The probability, then, of particle penetration is critical in determining clearance of particles from non-ciliated regions of the lungs. Phagocytosis by alveolar macrophages decreases the probability of particle penetration and aids clearance.

The crucial issue in a discussion of clearance rates is whether they are sufficiently great to balance deposition rates. It is the equilibrium level, or retention integrated over time and the physicochemical nature of the particle itself, that presumably determine probability of a pathological response.

In a recent report, Brain[225] applied the ICRP lung model[196] described in the Air Quality Criteria Document for Particulate Matter to predict retention of particles in lung compartments at different times. Three exposure patterns were considered in the predictions: acute pulse, continuous chronic and 40-hour work week exposures.

The results of the study underscore the importance of both size distribution and physicochemical composition in quantitation of particle retention. They clearly demonstrate that changes in particle size and solubility can alter the magnitude of retention and integrated exposure in some compartments even when identical masses of particulate are inspired. Although simplifying assumptions were made in preparation of the ICRP lung model, results of Brain's study reinforce the growing conviction that air quality standards must take into account size distribution and solubility of particulate material.

As for certain metallic air contaminants, there is more awareness of concentration gradients that exist in particulate samples as a function of particle size. Lee et al.[226,227] and others[228-230] have established that Pb, Cd, Zn, Cr, V, Ni, Mn and Cu are found at highest concentrations in the smallest particles collected from ambient air. To this list have been added As, Sb, Se and Tl, found by Natusch and Wallace[231] to be most concentrated in the smallest particles emitted from coal-fired power plants.

Unfortunately, little is known about matrix composition of small particles with which Fovic metals are preferentially associated. It is thought, however, that surface absorption or condensation of volatilized elements and organic compounds on to small particles is responsible for increased efficiency of respiratory deposition of these substances.[232] That this view has considerable significance in terms of environmental health is suggested by the fact that 1 μm MMAD particles are deposited predominantly in alveolar regions of the lung where absorption efficiency for most trace metals is 50 to 80%.[231] Similar conditions may prevail in the case of potentially carcinogenic organic vapors.

Because certain metals may be soluble in respiratory secretions, toxic properties of these substances may be manifested in lung parenchyma or airway epithelium or translocated so as to induce lesions in other sensitive tissues. Vanadium is an example of such a metal whose effects may show up through this mechanism. However, minimum time-concentrations of vanadium and other metal exposure that produce toxicity are not well understood. Also, toxicological assessment of metals that accumulate in the lung or other tissues present different problems than many other respiratory irritants because the relationship of tissue burdens to carcinogenesis, metabolic defects and mutagenesis or tetrogenesis is more difficult and time-consuming to assess.

5.1.6.2.5 Biological Respirable Particles--There are species of pollens, fungi, bacteria and viruses within respirable range in particle size. These biological particles are included among particles collected for measurement as respirable particles. However, it is difficult to characterize the concentration of these particles because of complexities involved in precise species identification. In the case of viruses and bacteria, concentrations may go low as to cause problems in measurement.

Respirable biological particles have received low priority by EPA because of lack of appropriate technology for their control that can be applied to the general population. However, biological respirable aeroallergens, microorganisms and certain other substances that may interact with biological tissues can be important in the etiology of immunological respiratory disease.

Certain paratoxic effects of gaseous atmospheric pollutants that involve increased susceptibility to airborne microorganisms have been reviewed recently by Coffin and Gardner.[233] These effects may be related to impaired pulmonary defensive capabilities and altered dynamics of respiratory air flow that change the pattern of regional deposition of inhaled particles. With regard to the latter, see Fairchild[224] and Lippmann, Albert and Peterson.[235]

5.1.7 Sulfur Oxides

5.1.7.1 Human Studies--The standards for SO_2 are shown in Table 5.30 and studies on which they were based when set on April 30, 1971 are presented in Table 5.31. These studies represented the best information available. Their limitations and shortcomings were recognized, but the Clean Air Act mandated that a standard be established. Included among this best available evidence for establishing an ambient air quality standard for SO_2 in 1970 were the following reports:

(1) Brasser, et al.[236] reviewed major episodes of air pollution in London and Rotterdam between 1952 and 1962. They indicated that excess mortality resulted when 24 hour mean levels of SO_2 exceeded 500 $\mu g/m^3$ (0.19 ppm) for a few days. Also, hospital admissions for respiratory illness as well as absenteeism increased whenever 24 hour mean levels of SO_2 reached 300-400 $\mu g/m^3$ for three-four consecutive days.

(2) Joosting[237] studied data from London episodes and determined that significant correlations between O_2 pollution levels and deaths or disease occur with 24 hour mean SO_2 concentrations of 400-500 $\mu g/m^3$ (0.15-0.19 ppm) when there is a high soot content.

(3) Carnow, et al.[238] studied a group of patients with chronic bronchitis. Substantial increases in illness were reported by persons 55 years and older with more severe bronchitis when concurrent or

proceeding daily SO_2 levels ranged from 119 to 249 μg/m^3 (.05-.09 ppm). The relationship was not observed among persons with less severe bronchitis or patients less than 55 years of age. During the period of study, TSP levels exceeded the 24 hour standard on about 15% of the days. So the effects observed may have been related to the combination of materials that the patients were exposed to.

(4) Wicken and Buck[241] studied mortality in two communities in England with contrasting pollution exposure levels. They found increases in lung cancer mortality in men and increases in bronchitis mortality in men and women associated with long-term mean SO_2 of 115 μg/m^3 (0.040 ppm) when compared with SO_2 exposure levels of 75 μg/m^3 (0.026 ppm). The high exposure community also experienced TSP levels of 160 μg/m^3 compared with 80 μg/m^3 in the low exposure area.

(5) Douglas and Waller[239] found increases in lower respiratory disease in London children to be directly related to a pollutant gradient that they were exposed to. Upper respiratory disease did not show a similar relationship. LRD was increased in areas where annual mean SO_2 concentrations were 130-148 μg/m^3 (.05-.06 ppm) or higher together with TSP levels of 91-138 μg/m^3 or higher.

6) Lunn et al.[243] observed increases in lower respiratory illness in England children associated with exposure to annual mean SO_2 levels of 194 μg/m^3 (.074 ppm) or higher and TSP levels of 177 μg/m^3 or higher compared with SO_2 and TSP levels of 109-134 and 70-78 μg/m^3 respectively.

To fill gaps in the information base as rapidly as possible, the Environmental Protection Agency maintains a continuing program of research to specifically assess adequacy of maximum permissible long-term or short-term exposure levels.

Table 5.30. PRIMARY NATIONAL AMBIENT AIR QUALITY STANDARDS FOR SULFUR OXIDE

Pollutant	National Primary Standard	
	Concentration ($\mu g/m^3$)	Averaging Time
Sulfur dioxide	80 $\mu g/m^3$ (0.03 ppm)	Annual arithmetic mean.
	365 $\mu g/m^3$ (0.14 ppm)	Maximum 24-hour concentration not to be exceeded more than once per year.

Table 5.31. INFORMATION BASE FOR ESTABLISHMENT OF NATIONAL PRIMARY AMBIENT AIR QUALITY STANDARD FOR SULFUR DIOXIDE

Adverse Health Effect	Concentration at Which Effect Was Observed		References
	Concentration ($\mu g/m^3$)	Averaging Time	
1. Increased mortality.	500 $\mu g/m^3$ (0.19 ppm)	24 hours	224,225
2. Increased hospital admissions with respiratory illness.	300-500 $\mu g/m^3$ (0.11-0.19 ppm)	24 hours	226
3. Increased frequency and severity of respiratory illness.	130 $\mu g/m^3$ (0.06 ppm)	Annual mean	227,228
4. Increased specific mortality.	130 $\mu g/m^3$ (0.06 ppm)	Annual mean	229

One of the primary problems in determining health effects of SO_2 continues to be development of an understanding of the manner in which this gas interacts with other substances in the atmosphere. Laboratory studies had demonstrated that the levels of SO_2 found in the ambient air are innocuous in an experimental situation until combined with other substances. Similar studies with animals demonstrated the high toxicities of sulfuric acid mists and various sulfate compounds that are products of the atmospheric transformation of SO_2.

Observed associations of adverse health effects in epidemiologic studies with ambient levels of suspended sulfates have supported these laboratory studies. Table 5.35 presents recent study results in a manner that relates adverse health effects to SO_2 exposure and suspended sulfate exposure. The studies referenced in Table 5.32 relate to a variety of health parameters.

An analysis of daily mortality in the New York metropolitan region between 1962 and 1966 indicated that SO_2 measurements contributed significantly to prediction of deaths. Mortality was 1.5% less than expected on 232 days with levels below 30 $\mu g\ SO_2/m^3$ and 2% greater than expected on 260 days with levels above 500 $\mu g\ SO_2/m^3$ after correcting for other factors.

In each of three New York neighborhoods, cold temperatures were directly related to increased symptom rates in persons with combined heart and lung disease. Elevated suspended sulfates were the only pollutant consistently aggravating symptoms. Daily sulfur dioxide and total suspended particulate concentrations could not be associated with symptom aggravation in the "heart and lung" panel that was most sensitive to variations in daily pollutant concentrations.

Table 5.32. ADDITIONAL SCIENTIFIC EVIDENCE

Adverse Health Effect	Concentration at Which Effect Was Observed			References
	Concentration $\mu g/m^3$		Averaging Time	
	SO_2 $\mu g/m^3$ (ppm)	SS $\mu g/m^3$		
1. Increased mortality.	300-400 (0.11-0.15)	NA	24 hours	230
2. Aggravation of symptoms in the elderly.	365 (0.14)	8-10	24 hours	231
3. Aggravation of asthma.	180-250 (0.07-0.09)	8-10	24 hours	232,233
4. Decreased lung function in children.	200 (0.075)	11	Annual mean	234,235
5. Increased acute lower respiratory disease in families.	90-100 (0.034-0.037)	9	Annual mean	236,237,238
6. Increased prevalence of chronic bronchitis.	95 (0.035)	14	Annual mean	239,240
7. Increased acute respiratory disease in families.	106	15	Annual mean	237,238

Best judgment estimates based on preliminary studies of 24-hour mean threshold levels for aggravation of cardiopulmonary symptoms in the elderly are 8-10 μg/m^3 of suspended sulfates.

Studies of daily asthma attack rates in the Salt Lake Basin showed that attacks were more consistently correlated with colder outdoor temperature than with any measured pollutant. An analysis of asthma attack rates compared to daily pollutant concentrations was carried out within two ranges of minimum temperature, 30 to 50°F and greater than 50°F. Virtually no relationship between sulfur dioxide and attack rates appeared.

Total suspended particulates and suspended sulfates were positively correlated with daily asthma attack rates. A higher frequency of asthma attacks was observed at the same daily total suspended-particulate concentration when a high sulfate fraction was present in the atmosphere. It then appears that sulfate levels were a stronger determinant of asthma attack rates than total suspended particulates.

In New York, also, asthma attack rates were more consistently associated with daily suspended sulfate levels than with either sulfur dioxide or total suspended particulates.

In the opinion of the authors, best judgment estimates of the 24-hour mean levels of SO_2 that might serve as precursors of significant ambient SO_4 concentrations were 180-250 μg/m^3.

Ventilatory function of elementary school children diminished as measured by 0.75-second forced expiratory volume in areas of elevated exposure to sulfur oxides. In New York only older children (ages nine to 13 years) who had been exposed to substantially elevated pollutant concentrations for the first five to 10 years of life showed evidence of reduced ventilatory function. The best available estimates of these previous annual average exposures were as follows: sulfur dioxide, 131 to 435 $\mu g/m^3$; total suspended particulates, 75 to 200 $\mu g/m^3$; suspended sulfates, 18 to 28 $\mu g/m^3$. The best judgment estimate of a threshold level for SO_2 was approximately 200 $\mu g/m^3$.

In a Cincinnati study of ventilatory function in children, suspended sulfates emerged as a pollutant of particular concern. Sulfur dioxide concentrations were at or below the moderate level of 57 $\mu g/m^3$ during the time of testing permitting suspended sulfates to be assessed in the relative absence of sulfur dioxide. Ventilatory function in children exposed to suspended sulfate concentrations of about 9.5 $\mu g/m^3$ was lower than that of children exposed to concentrations of about 8.3 $\mu g/m^3$. It was the authors' best judgment that eight or nine years of exposure to about 10 to 13 $\mu g/m^3$ of suspended sulfates might reduce ventilatory function. If these suspended sulfate exposures were accompanied by exposures to about 200 to 250 $\mu g/m^3$ of sulfur dioxide and about 100 to 150 $\mu g/m^3$ of total suspended particulates, further reductions in FEV 0.75 might be expected.

Lower respiratory disease studies conducted in the Salt Lake Basin and Rocky Mountain areas found no significant association between total lower respiratory disease and pollution for children whose parents had been residents of their communities for less than three years. For single and repeated episodes of croup and repeated episodes of any lower respiratory disease, families of children who had lived three or more years in the high exposure communities reported more illness among all ages of children from 0 to 12 years than did their counterparts in less polluted communities.

Best judgment estimates of the threshold levels for increases in acute lower respiratory tract infections in children were three years of exposure to 95 $\mu g/m^3$ of sulfur dioxide, 102 $\mu g/m^3$ of total suspended particulates and 15 $\mu g/m^3$ of suspended sulfates.

Chronic bronchitis rates in CHESS areas showed a consistent pattern of excess among residents of more polluted communities.

In the Salt Lake Basin, male smokers and non-smokers showed an excess of chronic respiratory disease whether defined in terms of bronchitis prevalence or severity scores. Chronic bronchitis rates and severity scores were higher among male and female smokers, non-smokers and ex-smokers from more polluted areas than they were in comparable groups from less polluted areas.

Among young white military recruits in the Chicago area, the contribution of air pollution was relatively much less than that of cigarette smoking. However, there was evidence that even among these young inductees, respiratory symptoms were more prevalent among persons from more polluted communities.

Best judgment estimates of the threshold levels for increase in prevalence of chronic bronchitis in adults were six years of exposure to 95 $\mu g/m^3$ of sulfur dioxide, 100 $\mu g/m^3$ of total suspended particulates, and 14-15 $\mu g/m^3$ of suspended sulfates.

Studies of total acute respiratory disease among family members in Chicago and New York showed that, with the exception of fathers, who often have greater occupational exposures and daily changes of exposure due to place of work, a consistent excess of acute respiratory disease was reported among family members living in more polluted neighborhoods.

Best judgment estimates of the threshold levels for increase in frequency or severity of acute respiratory illness in families are three years of exposure to 106 $\mu g/m^3$ of sulfur dioxide, 151 $\mu g/m^3$ of total suspended particulates and 15 $\mu g/m^3$ of suspended sulfates.

Best judgment estimates of the exposure threshold for adverse health effects are given in Table 5.33. The margins of safety are included in the air quality standards in Table 5.34. And estimates of the population at risk are presented in Table 5.35.

5.1.7.2 Animal Studies--The health effects of sulfur oxides have recently been critically reviewed in four major reports:

1. Summary report on adverse health effects related to sulfur oxides exposure, Environmental Protection Agency, Research Triangle Park, N. C., September, 1973. Unpublished.
2. ERC/RTP Task Force report on sulfates and sulfuric acid aerosols, October, 1973. Unpublished.
3. Toxicology of sulfur dioxide decay products by Lewis et al.[253]
4. A review of the toxicology of oxidation products of sulfur dioxide by M. O. Amdur.[254]

Information in these documents help provide the basis for Air Quality Criteria for Sulfur Dioxide. For information published before 1972, readers should refer to the above referenced documents. In the two years since these documents were compiled, only a limited amount of new information has been obtained that contributes significantly to understanding of toxicologic properties of sulfur oxides.

Recent research on sulfur oxides has continued to demonstrate that the respiratory tract is the principal organ system affected. The

Table 5.33. BEST JUDGMENT THRESHOLD ESTIMATES FOR HEALTH EFFECTS OF SULFUR OXIDES

Adverse Health Effect	Best Judgment Threshold Estimate		
	Concentration µg/m^3		Averaging Time
	SO_2	SS	
1. Aggravation of cardio-respiratory symptoms or lung symptoms in elderly patients with related illness.	365	10	24 hours
2. Increased mortality.	350	NA	24 hours
3. Aggravation of asthma.	200	8-10	24 hours
4. Reduced lung function.	200	11	Annual mean
5. Increased frequency or severity of lower respiratory illness.	91	9-12	Annual mean
6. Increased prevalence of chronic bronchitis.	95	14	Annual mean
7. Acute respiratory disease.	106	12	Annual mean

Table 5.34. SAFETY MARGIN INCLUDED IN SULFUR OXIDE STANDARD

	Adverse Effect	Threshold Concentration $\mu g/m^3$	Primary Standard $\mu g/m^3$	Safety* Margin %
1.	Aggravation of heart or respiratory symtoms in the elderly.	365	365	0
2.	Increased mortality.	350	365	0
3.	Aggravation of asthma.	200	365	0 (-45)
4.	Reduced lung function.	230	80	187
5.	Increased lower respiratory illness.	91	80	14
6.	Increased chronic bronchitis.	95	80	19

$$\text{*Safety Margin} = \frac{\text{Threshold Concentration - Standard}}{\text{Standard}} \times 100$$

Table 5.35. SIZE OF POPULATION AT POTENTIAL RISK OF POLLUTANT-INDUCED EFFECT

Adverse Effect	Expected Frequency of Adverse Effect in the Population (Rate per 100)	Potential Size* of Population at Risk
Chronic bronchitis.	10% of adult population	8,400,000
Asthma.	3%	4,200,000
Chronic heart illness.	5% of adult population	4,200,000
Susceptible to respiratory infection.	100	140,000,000

*Assumes a U.S. population of 200,000,000 and 70% of total population living in urban areas of increased pollution.

available data on comparative toxicity of sulfur oxides indicate that sulfur dioxide is only a mild respiratory irritant, while specific sulphate and sulfuric acid aerosols are more potent respiratory irritants. The importance of particle size as well as mass concentration to toxicity of sulfur dioxide aerosols is of paramount importance. Experiments demonstrating this point have been reviewed recently.[254]

Most recent studies of sulfur-oxide toxicity have been concerned with sulfur-oxide aerosols or sulfur dioxide in combination with an inert particulate aerosol. The importance of high relative humidity to enhancement of the effect of sulfur dioxide and sodium chloride aerosol has been demonstrated through sensitive repsiratory physiologic responses.[255] These compounds (SO_2- 1 ppm and sodium chloride 1 μg/m^3) alone or in combination caused no effect on pulmonary airflow resistance of guinea pigs at low relative humidity (40%). However when the relative humidity was increased to $\geq$80%, a 50% increase in pulmonary airflow resistance developed. The increase in relative humidity resulted in an increase in aerosol size and production of an acid aerosol that are thought to be important events in the production of an irritant aerosol leading to increased pulmonary airflow resistance.

A concentration of 3020 μgm/m^3 H_2SO_4 (1.8 u CMD size) that has been shown to increase pulmonary airflow resistance in guinea pigs also produces an increase in total respiratory particle deposition in guinea pigs.[256] This increased particle deposition occurred primarily in the nasopharynx, i.e., a proximal shift in the normal pattern of regional deposition of radio-labelled bacterial aerosol occurred. Dose-response experiments revealed that even at a concentration of 30 μgm/m^3 (0.25 u CMD size) a proximal shift in the pattern of respiratory particle deposition occurred. But in this instance the shift was to the trachea. These results suggest where the site of action is of H_2SO_4 aerosols of this mass concentration and particle size.

Particle deposition in the respiratory tract is correlated to airflow dynamics in this system. The suggestion has been made that these results reflect a subtle patho-physiologic consequence to altered respiratory airflow resistance. So these results provide added significance to respiratory physiologic responses that are commonly used in air pollution health effects studies.

A concentration of 15 $\mu g/m^3$ of H_2SO_4 (2.5 u CMD size) for 90 minutes per day for four consecutive days induced a reduction in the physical clearance of radio-labelled streptococcous particles deposited in the nose and lungs of mice.[245] No effect was demonstrated on the clearance of viable streptococci from these same tissues. However, no effect on physical clearance of streptococci was observed at a mass concentration of 1.5 $\mu g/m^3$ H_2SO_4 (0.8 u CMD size). These data suggest that alterations in respiratory particle deposition and pathyphysiologic consequences of these alterations are a more sensitive index of response to H_2SO_4 inhalation than mucociliary clearance of particles.

Busey et al.[258] have demonstrated that chronic exposure (78 weeks) of guinea pigs to a combination of fly ash (0.55 $\mu g/m^3$) and H_2SO_4 aerosol produced inflammatory lesions in terminal bronchioles of the lung characterized as moderate hyperplasia of the epithelium.

The only alteration in respiratory physiologic measurements was a small increase in respiratory airflow resistance that might be associated with histopathologic lesions. The results of this experiment are important because a much higher concentration of sulfur dioxide did not produce any health effect.[259-261] A combination of SO_2 (up to 5 ppm) and fly ash (0.5 $\mu g/m^3$ - size 2.6 - 3.4 u MMD) exposure for 78 weeks did not induce any respiratory physiologic or histopathologic effects in monkeys or guinea pigs.[262]

Zakower[263] has observed small changes in immunologic responsiveness of rats chronically exposed to sulfur dioxide and carbon dust. These observations have not been confirmed or the pathophysiologic consequence of this effect demonstrated.

5.1.8 Mercury

Several recent animal exposure studies using methyl mercury given in repeated oral doses over relatively long time periods show that a "no-effect" level for development of neurological signs and/or histopathological evidence of mercury poisoning is from 0.03 mg/kg body weight (monkeys, cats) to 0.1 mg/kg body weight (calves).

Daily oral doses of alkyl mercury compounds as small as 0.4 mg/kg body weight have produced neurological disorders in rabbits, cats and dogs. Daily oral doses of 0.25 mg/kg body weight of methyl mercuric chloride given throughout most of the gestational period caused increased abortions and fetal abnormalities in cats. Similarly, levels above 0.3 mg/kg given during gestation increased fetal abnormalities in rat fetuses.

Most animal experiments were carried out with daily dose levels much higher than the foregoing experiments and the most chronic exposure found was that of monkeys that were exposed for two years. Low level, long-term exposures were notably absent.

Behavioral changes have been produced in rodents where no histological lesions were found from single oral doses of methylmercuric chloride. The relatively high 25 mg/kg dose level was required since doses at 20 mg/kg level did not produce significant changes.

Ikeda[264] fed methyl mercuric chloride (MMC) to four groups of five male monkeys each for two years. Groups were made up of three Macaca Mulatta and two Macaca Irus each. Levels used were 0.01, 0.03, 0.1, 0.3 mg/kg/day plus a control level. In the two highest levels (0.1 and 0.3 mg/kg/day), toxic neurological signs appeared at 62 and 182 days respectively when total amount of MMS ingested was 15.3 and 15.9 mg/kg. No neurological signs were noted in the other groups although animals fed at the 0.03 mg/kg level ingested a total of 18.4 mg/kg MMC by the end of two years. No significant alterations occurred in hematological or biochemical parameters tested in the two lower dose groups. The mercury content of hair showed good correlation with the daily dose of mmc. This study is still in progress.

Takeuchi[265] reported on total amounts of methyl mercuric chloride (MMC) necessary to produce poisoning similar to Minamata disease. In cats, the total dose was 20.6 to 25.7 mg/kg at a daily level of 1.5 to 2.0 mg/kg. In rats, total dose was 100 to 200 mg/kg at a daily level of 5 to 10 mg/kg. Extrapolating from these figures to man is a total dose of 20 mg/kg.

Khera[266] fed pregnant cats orally with doses of methyl mercuric chloride (MMC) from the tenth day to the 58th day of induced (gonadotrophin) pregnancy to determine teratogenic effects. The results were:

Dose Level	Number	Results
0	7	
0.03 mg/kg	5	No signs of poisoning detected in dams.
0.83 mg/kg	6	No signs of poisoning detected in dams.
0.25 mg/kg	9	Increased abortions and fetal anomalies.
0.75 mg/kg	4	Vomiting, ototoxia and death of dams within 32 days post exposure.

Minimal or no embryopathic effects were noted at the two lowest levels. The 0.03 mg/kg dose was considered the "no-effect" level. This correlates well with the IDEDA[264] experiment using monkeys where the feeding period was two years.

Magos[267] studied cumulative effects of oral methyl mercury dicyandiamide (MMD) on rats. Female albino rats were divided into the following three groups:

I. 3.36 mg/kg for five days/week for 16 doses N=14
II. 1.68 mg/kg for five days/week for 34 doses N=12
III. 0.84 mg/kg for five days/week for 59 doses N=16

Group I showed weight loss after the fourth dose and neurological abnormalities after the twelfth dose.

Group II lost weight after the 24th dose when four of the six animals remaining were ototoxic.

Group III increased in weight throughout the experiment but two of these animals showed slight ototoxia.

All groups exhibited histopathological changes in the kidney and cerebellum.

Irukayama[268] reported on short-term (10-90 days) multiple oral-exposures to methyl mercury that produced neurological disorders in rabbits, cats and dogs. The daily intake of MM was 0.4 to 1 mg/kg and the total intake in these species between 10 and 20 mg/kg. To produce similar signs in rats required a total dose of approximately 100 mg/kg indicating the higher degree of resistance of this species.

Post[269] recorded behavioral changes in the following three groups of young rats (force-fed a single dose of methyl mercuric chloride [MMC]):

Group I	15 days old	20 mg/kg	N=15
Group II	21 days old	20 mg/kg	N=15
Group III	60 days old	25 mg/kg	N=45

The differences in behavioral measurements in Groups I and II vs. controls were small or statistically insignificant. Behavioral changes in Group III were significant, however. The authors state that significant behavioral changes in Group III could result from higher doses of MMC or age differences. Since no histopathological changes were found in any group, the authors conclude that behavioral testing was the more sensitive indicator of mercury poisoning.

In a study by Fukuda,[270] two of six rabbits that were exposed to an average concentration of 4 mg/m^3 of mercury vapor for six hours a day, four days a week, for 13 weeks, developed a fine tremor and clonus in the fore- and hind-legs. (This level is 4000 $\mu g/m^3$, a relatively high exposure.) Analysis of CNS tissue showed mercury levels of 0.8 to 3.9 μg/g wet tissue.

Beliles[271] found fine tremors in the fourth week in rats repeatedly exposed to mercury vapor at: 17 mg/m^3 for three hrs/day, five days/week for four to five successive weeks. Histological changes in the CNS were also present.

Charbonneau[272] exposed two groups of cats to 0.25 mg/kg/day methyl mercury for 12 to 14 weeks. One exposed group received methyl mercuric chloride in gelatin capsules. The other group received methyl mercury-contaminated fish. A control group received uncontaminated fish. Clinical signs of neurological abnormality developed in both exposed groups between 55 and 96 days. At that time, total methyl mercury ingestion was between 14 and 24 mg/kg.

Tissue mercury content and pathologic changes were similar in both exposed groups of treated animals. Lesions were found in the cerebellar vermis and the cerebral cortex.

Pre-test blood mercury concentrations in the cats were considerably higher than background value for humans, possibly reflecting the dietary history of the cats. Cats seem similar to other species, including man, that develop clinical signs of methyl-mercury toxicity when brain concentrations are in the range of 10 ppm.

Gale[273] injected golden hamsters with mercuric acetate (inorganic mercury) and phenylmercuric acetate (organic mercury) on the eighth day of pregnancy and sacrificed them on the 12th or 14th day of pregnancy to study potential teratogenic effects in this species. Mercuric acetate levels used were 2, 3 and 4 mg/kg, while phenylmercuric acetate was given at 5, 7.5, 8 and 10 mg/kg. All levels of mercuric acetate and all but the lowest level of phenylmercuric acetate produced resorption rates significantly above control values. Both compounds produced the same changes in embryos.

Embryonic growth rate was retarded one to two days and abnormal fetuses had sub-cutaneous edema. Finding of similar results from exposure to organic and inorganic mercurials may be due to rapid metabolism of organic mercury into inorganic form in both liver and kidneys.

Gale[274] injected pregnant hamsters intravenously with mercuric acetate in combination with either cadmium sulfate or zinc sulfate on the eighth day of gestation. (Dose levels of each compound were either 2 or 4 mg/kg.) On the 12th or 14th day of gestation, embryos and implantation sites were examined for malformations and resorptions. The detrimental effects of Hg + Cd were much worse than those of the Hg + Zn combinations. Manifestations of toxicity in dams were directly proportional to the mercuric acetate dose. Animals that received the higher mercury dose (4 mg/kg) showed more severe toxic effects than any of the Hg + Cd or Hg + Zn combinations.

In a study by Spyker,[275] methyl mercury dicyandiamide (MMD) was injected into pregnant mice on the seventh or ninth day of gestation at levels of either 4 or 8 mg/kg. The number of apparently normal neonates killed by the dam was significantly increased if offspring were prenatally exposed to MMD. Additionally, open-field testing at 30 days of age revealed significant differences in latency, backings, defecations and urinations.

In another study by Spyker,[276] a total of 667 female mice of two strains (129/Sr-S1 and A/J) were given I.P. injections of Methyl mercury elicyandiamide (MMD) on one of days six to thirteen of gestation and 2,280 implantation sites were examined on day 15 or 18. Dose levels used were 0, 2, 4 or 8 mg MMD/kg. The 8-mg/kg dose produced growth retardation in both strains and was 88% embryo-lethal when given on days nine to 13 in strain 129.

This dose level was not embryolethal in strain A. But it did cause cleft palate in this strain when injected on days nine to 13. Examinations of fetuses from strain 129 on day 15 revealed 52% of embryos had brain, palate or facial abnormalities. Off-spring that appeared normal showed significant behavioral differences when submitted to battery tests.

Klein[277] exposed 25-day-old rats to sub-lethal oral doses of mercuric chloride at either 5 or 7 mg/kg daily for two weeks prior to active-avoidance training. Klein's results indicate that mercuric chloride administration significantly impaired active-avoidance acquisition without influencing either escape latencies or general physiological condition.

Kawabe[278] gave methyl mercury chloride orally to pregnant mice on the tenth day of gestation at dose levels of 0.1, 0.2, 0.3, 0.5, 1.0, 1.5 and 2.0 mg/kg. Fetuses were removed and examined on the 15th gestational day. At levels of 0.5, 1.0, 1.5 and 2.0 mg/kg the number of dead fetuses and resorptions were increased. Levels of mercury that produced abnormalities in this experiment substantially agree with the experiments of Spyker (mice) and Khera (cats).

Munro[279] gave groups of eight to 10 male Wistar rats daily oral doses of methyl mercuric chloride (MMC). Clinical signs of mercury intoxication appeared in all groups but the lowest dose level. Pathological changes occurred in the nervous system of all treated rats involving Wallerian degeneration of sensory nerves, swelling with loss of myelin in the posterior white column of the spinal cord, secondary loss of nerve cells in dorsal root ganglia and atrophy of the cerebellar vermis from loss of granular cells and some Purkinje cells. The results were:

Dose	Appearance of Clinical Signs
10 mg MMC/kg/day	7 days
5 mg MMC/kg/day	14 days
1 mg MMC/kg/day	65 days
0.5 mg MMC/kg/day	120 days
0.05 mg MMC/kg/day	No signs at 280 days

Herigstad[280] fed six four-week-old male Holstein-Friesian calves methyl mercury that produced neurological signs and histopathologic changes of mercury poisoning at levels as low as 0.2 mg/kg/day at 90 days exposure.

Iverson[281] induced overt clinical signs of mercury intoxication in guinea pigs after daily dosing for nine days at 5 mg methyl mercury/kg.

Tatetsu[282] gave 5 mg/kg dimethyl mercuric sulfide orally daily to pregnant rats during two to three weeks of pregnancy producing degenerative changes in the brains of their newborn.

Suzuki[283] produced neurological signs in mice at dietary levels of 10 μg of methyl mercury per gram of feed. This group did not show any loss of body weight or neurological symptoms until the 41st day of feeding. The most sensitive neurological sign was noted at a methylmercury concentration of 10 μg per gram of brain.

Iverson[284] found the LD_{50} (14) for methyl mercuric chloride in female guinea pigs to be 5.5 mg/kg I.P. and 16.5 mg/kg P.O. The tissue distribution of a single orally-given dose was studied with the following results: Kidney>Liver>Spleen>Heart>Brain. A biphasic excretion pattern was common to most organs except the kidney. Half-times were t_1 = two to three days and t_2 = 15-16 days for most tissues. Kidney turnover rates were much slower.

Newberne et al.[285] fed rats fish-protein concentrate (FPC) as part of their diet to provide 20% protein for five generations. Average total mercury content of FPC samples was 0.22 ppm with more than 90% in the form of methyl mercury. Over the two-year feeding period, there was no evidence of effects on growth, development, reproduction or behavior throughout the five generations. Histologic examination revealed no lesions of the brain, kidney or liver caused by the diet. The average weekly intake of the animals was 12 μg/kg per week.

Singhal et al.[286] injected young male rats with 0.4 or 4.0 mg methyl mercury/kg/day for 45 days and produced a significant decrease in liver weights at both doses. Gluconeogenic enzyme activities increased in nearly all enzymes examined at both dose levels. Elevated blood glucose and urea along with reduced liver glycogen content occurred at both dose levels. Withdrawal of mercury exposure to 4 mg/kg/day for 28 days post-exposure generally failed to reverse observed metabolic changes in hepatic and renal carbohydrate metabolism.

Lucier et al.[287] found that subcutaneous injection of male rats with methyl mercury hydroxide at 2.5-10.0 mg/kg/day for two days decreased hepatic mixed-function oxidase activity and microsomal cytochrome P-450 content by approximately 50%. Oral administration with drinking water of MMH of approximately 0.7/mg/kg/day for 30 days or 1.0 mg/kg/day for 17 days cytochrome P-450 and aminopyrine demethylase were decreased by only 20% approximately.

Klein et al.[288] injected rats daily for five days with 2-10 mg/kg of methyl mercury hydroxide (MMH). Only the highest dose group had weight loss. No CNS damage was noticed. Focal necrosis of kidney tubular epithelial cells were noted by day six. These studies identify the kidney as an early target in MM intoxication and suggest that biotransformation of MMH into inorganic mercury may produce part of the pathological changes noted.

Fowler et al.[289] gave rats 55 ppm Hg (as methyl mercury hydroxide) in drinking water for four weeks. Proximal tubule cells of kidneys were found to contain swollen mitochondria with dense granual cytosomes. Sodium phenobarbital, a microsomal enzyme inducer, given weekly during MMH administration, prevented these histologic changes (possibly by stimulating the metabolism of MM and reducing renal mercury levels and attendant nephrotoxic effects).

Hastings et al.[290] found that injection of 10 mg MMH/kg for two days reduced serum cholinesterase activity by 50% in male and female rats, but had no effect on brain acetylcholinesterase levels.

Khera et al.[291] intubated pregnant mice with CH_3 Hg Cl at doses of 0.001 to 10 mg Hg/kg/day from day six to 17 of gestation. Doses of 5 mg/kg/day caused 100% stillbirths or neo-natal death but no maternal toxicity. Doses of 1 mg/kg/day caused a low incidence of delayed cerebellar differentiation of progeny and depressed activity of cerebellar enzymes. Young female rats were fed methyl mercuric chloride in the diet at levels of 0.002 to 0.25 mg Hg/kg/day until sexually mature and then mated to untreated males. Treatment continued throughout pregnancy, delivery and weaning. At weaning, half of the progeny remained on the experimental diet and others reverted to a control diet. All animals were subsequently mated and sacrificed on day 20 of gestation.

Long-term feeding of parent female rats with diets containing up to 0.25 mg/Hg/kg/day for 122 days had no discernible effect on growth, behavior or pregnancy. No effects were seen at any dose level on the F_2 fetal weight, abnormalities, gross or microscopic histology of brain and spinal chord or viability. A variable incidence of ocular lesions was dose-related.

5.1.9 Beryllium

Significant animal studies conducted since the classification of beryllium as a hazardous pollutant are reviewed briefly.

A soluble tissue extract prepared from animal and human lung connective tissue sensitized normal guinea pigs to subsequent exposure of beryllium as assayed by the skin reaction, macrophage migration inhibition factor and lymphotoxin production. Greater than 50% of animals with tuberculosis, berylliosis or coal pneumoconiosis exhibited some evidence of cell-mediated sensitivity to appropriate soluble tissue extract.[292]

Mice and guinea pigs treated with metyrapone to alter adrenal function had a more severe reaction to beryllium ($BeSO_4$ or BeO via transthoracic or intratracheal injection) than control animals as indicated by weight loss, metal-ion shift and elevation of serum enzymes, all signs of systemic disease. Response to altered adrenal function has been seen in human cases, but never before demonstrated in animals.[293]

Injection (I.p) of 0.8 mg $BeSO_4$/kg into rats induced a maximum elevation of liver acid phosphatase after eight hours, and elevation of the serum isocitric dehydrogenase, glutamic-pyruvic transaminase and glutamic oxalacetic transaminase activities 48 hours after injection. The serum lactic dehydrogenase was not elevated at any time.[294]

Clary et al.[295] studied the long latent period, sometimes 15 or more years, between onset of the disease and last exposure to beryllium. The latent period may be explained on the basis of beryllium accumulation in a latent form in the lyosome. This latent period could persist for years until the general decline in adrenal output due to aging was combined with adrenal stress. Under these conditions, especially if the adrenal reserve was also low, adrenal output may not be adequate to meet all needs. The lyosomal instability could result, initiating onset of beryllium disease.

After i.v. injection of ^{7}Be the biological half-times were 1210, 890, 1770 and 1270 days in mice, rats, monkeys and dogs respectively, compared with the 540 day value cited by the ICRP.[296]

Partially hepatectomized rats given 15, 30 or 60 μ moles $BeSO_4$/kg showed liver necrosis when examined 48 hours after i.v. injection. The abolition of mitoses was observed after 20 or 16 hours in animals treated with 30 μ moles $BeSO_4$/kg 8, 12 and 22 hours after partial hepatectomy.[297]

Jacques and Witschi[298] found that beryllium did not prevent induction of aryl hydrocarbon hydroxylase by methylcholanthrene. The authors concluded that it is unlikely that beryllium could act as a pulmonary cocarcinogen by interfacing with the metabolis of carcinogenic polycyclic hydrocarbons in the lung.

Delayed-type hypersensitivity bo beryllium was demonstrated in guinea pigs sensitized with $BeSO_4$ by the skin test using $BeSO_4$ and Be-guinea pig albuminate, but not with beryllium hydrgencitrate or beryllium-aurintricar-boxylate.[299]

Guinea pigs sensitized to beryllium by i.d. injections had skin reaction to beryllium salts. Sensitivity to beryllium was passively transferable by peritoneal exudate and spleen cells. Macrophage migration-inhibitory factor (MIF) was produced in approximately 74% of guinea pigs with positive skin tests. Six out of seven chronic berylliosis patients showed MIF production. There was systemic involvement of the alveoli, bronchiole muscles and spleen due to berylloisis.[300]

Schneider et al.[301] found that a nine-fold increase in the rate of bone formation occurred in the beryllium-injected tibia during the first four weeks. The rate declined to normal during the last four weeks. Pathological defects were prominent in newly-formed bone. Some areas were deficiently mineralized and had an increased number of resorption spaces.

Slonim et al.[302,303] found that the amount of beryllium concentrated in guppies and fry was influenced by concentration of beryllium sulfate in the surrounding solution, by fish size (inversely) and, to a lesser extent, by exposure period; but not by fish age, solution buffering or water hardness. Beryllium uptake was highest in the gastrointestinal tract and kidneys, but varied greatly among guppies exposed to the same conditions. Beryllium lethality in fish may not depend on amounts concentrated in fish, but on its effects on a particular target organ or cellular or subcellular component.

The variability in beryllium uptake observed in expired fish was great, indicating that amounts absorbed in the body are not important determinants of beryllium lethality.

Vacher[304-306] found that contact of beryllium with skin produces a delayed-type hypersensitivity reaction in guinea pigs, while parenteral administration of beryllium produces tolerance. The immune response to beryllium is associated with different forms of beryllium, i.e., immunogenic (bound to skin constituents) and tolerogenic (freely diffusible). Low dose tolerance was achieved by i.p. injection of a very low dose of beryllium (4.78 μg/kg) and high dose tolerance by i.v. injection of 400 μg/kg. $BeSO_4$-induced blockage of the reticuloendothelial system (RES) is due to "non-diffusible" phosphate fraction formed after i.v. injection of sulfate. This blockage does not appear to result from a cytotoxic effect since injected beryllium phosphate, five times less toxic than $BeSO_4$, is active at doses 100 times lower than toxic doses. Blockage and cytotoxicity of beryllium do not appear to be linked to the same mechanism. RES blockage is thought to occur as a result of saturation of absorption sites on phagocytic cells.

Intravenous injection of beryllium phosphate and zymosan, before or during development of adjuvant-induced polyarthritis in the rat, decreased inflammatory reactions in the paw injected with adjuvant. The observed effects appear to be related to a nonspecific activation of the phagocytic cells with possible lyosomal changes that lead to production of substances demonstrating the observed properties.

Vasil[307] found that the nucleo-protein fraction of lungs of rats with experimental berylliosis contains six new antigens (as revealed by immunoelectrophoresis). Some of these antigens contain beryllium.

5.1.10 Asbestos

The association of impaired human health with industrial exposure to asbestos is well known. Many hundreds of cases of asbestosis (fibrosis of the lung) and pulmonary cancer associated with mining, milling and manufacturing of asbestos and asbestos products have been documented. The subject has been reviewed many times recently.[308-313]

An attempt will be made here to give a cogent story on the biological experimentation, to discuss possible implication of air pollution of general or point source exposure to commercial asbestos and the possible hazard of exposure of human beings to asbestos-like fibrils that are generated inadvertently from mining and quarrying.

There is little evidence that light exposures such as might be encountered in ambient air produce asbestosis or pulmonary carcinoma in human beings. These conditions have been consistently reported only from heavy industrial contact with asbestos. However, the discovery of association of a unique tumor, mesiothelioma of the pleura of peritoneum, with very low exposure, or after casual contact with chrysotile asbestos, usually after a long period of latency, has raised a question about risk due to air pollution.

Many of these exposures had come from such things as living in homes occupied by asbestos workers or living in vicinity of asbestos factories and mills. In some cases mesiothelioma developed as long as 30-40 years after any known contact. While most of the South African cases were attributable to chrysotile asbestos,[314] mesothelioma was found in the USA in workmen working solely with amosite.[315] In Finland no mesothelioma is associated with the prevalent anthophyllite asbestos.[316]

The following summary points have been listed for the epidemiology of asbestos:[317]

(1) All major types of asbestos can cause lung cancer, although there are clear differences in risk with type of fiber and nature of exposure. Since exposure and response to asbestos are related, there is no excess risk when occupational exposure has been low.

(2) All commercial types of asbestos except anthophyllite may cause induction of mesothelioma. The risk is greatest with crocidolite, less with amosite and apparently less with chrysotile. With the last two, there seems to be a greater risk in manufacturing than in milling.

(3) There is evidence of an association of development of mesotheliomas with air pollution near crocidolite mines and factories using mixed fibers. There is no excess risk from air pollution near chrysotile and amosite mines.

(4) There is, at present, no evidence of any cancer risk to the general public from asbestos in air, water, beverages, food or in fluids used for administration of drugs.

(5) Cigarette smoking enhances the risk of developing bronchogenic cancer in workers exposed to asbestos. No association between cigarette smoking and development of mesothelioma has been demonstrated.

(6) Pleural plaques are associated with past exposure to all commercial types of asbestos although not all pleural plaques are related to asbestos.

The amphiboles are an important group of rock-forming minerals estimated to comprise as much as 3% of the earth's crust and associated with both igneous and metamorphic rock. They are divided geologically into three sub-groups: (1) iron-magnesium amphiboles, (2) calcium amphiboles and (3) alkali amphiboles.

The first sub-group contains grunerite, the commercial asbestos form of that is termed "amosite." Massive amounts of grunerite and other amphiboles of non-commercial asbestos quality occur in the United States and are mined inadvertently because of association with other minerals that have commercial value, e.g., the Reserve Mining Company's taconite ores from the Peter Mitchell Pit. As a result since amphibole ore is estimated to comprise about 3% of the earth crust, they are present as matrices in many mining, quarrying, tunneling or other hard rock activities where inadvertent exposure may occur both occupationally and environmentally in the surrounding community.[318]

It is possible that even agricultural processes in areas where surface outcrops of asbestiform rock occur may pose a risk to human health.[319]

There is a growing body of evidence suggesting that health effects associated with exposure to asbestos may not be unique to commercial forms, but may also be associated with asbestos-like fibers found in other rocks and even man-made fibers.[320-324] It is now known that the external gross appearance of the mineral may not be the determinant. It may be its microfibrillar nature after crushing or grinding.

The toxicity potential of the silicate mineral may then be related to their proclivity to form micro-crystals of a certain configuration when crushed and ground. It is likely, then, that a mode of toxicity formerly thought to be associated only with asbestos may be present to a greater or lesser degree in fibrous amphiboles of non-asbestos commercial quality.[325]

Recent reports on exposure of rats to various forms of asbestos indicate that, while there appears to be a time-dependent dose response in tumor incidence, no significant difference was noted among various amphibole asbestos when compared to chrysotile from both South African and Canadian sources.[326]

It would appear possible that pleural and peritoneal mesothelioma and possibly other disease of man can result from exposure to amphibole of non-commercial asbestos quality.

"Asbestos bodies" are prevalent in the general population of city dwellers as is well know. But the question of association of these bodies with asbestos fibers is a moot point since it is known that similar fibers of other kinds can develop into these structures after residence in the tissue. However, critical examination of 28 human lungs from autopsy material obtained in N.Y.C. by means of appropriate E.M. technique has revealed chrysotile fibers in all lungs.[327] Similar studies in London have shown that chrysotile fibers are found in 80% of the specimens of lung included in recent surveys of post-morten material. (See Tables 5.36 and 5.37.)

The discovery of asbestos fibers in lungs of human beings not occupationally exposed indicates potential risk to the general public. More surveys are needed to properly to assess this risk. However, since asbestos is a chemical now common only because of widespread commercial use in the past 100 years or so and there has been a thousand-fold increase in its use in the 20th century, the risk appears to be growing.

Studies under way on occurrence of asbestos fibers in the ice cap in Greenland suggest that there has been an increase in fiber deposition since the 20th century began. As such, the latency associated with prime low-level lesion (mesotheliomi) and apparent increase of potential exposure from air pollutants cannot be disregarded.

5.1.10.1 Biological effects of Asbestos--The principal effects of asbestos exposure in people that are reproducible in experimental animals include pulmonary fibrosis and carcinogenicity.

5.1.10.1.1 Fibrogenesis--Chrysotile asbestos was shown to produce fibrosis as early as 1925.[314] Amosite and crocidolite have also been shown to have this property.[328] It now appears that most types of asbestos are fibrogenic. Long fiber length is considered important to fibrogenesis according to some investigators. But others have found short fibers to be fibrogenic.

The exact mechanisms that initiate various asbestos lesions are still unknown. It is possible that the mechanisms for different lesions (fibrosis, pulmonary, carcinoma and mesothelioma) are all different. Fibrosis (asbestosis) is usually related to massive dose exposure and has the shortest period of latency so that asbestos is associated with all forms of asbestos fibers in industrial exposure. The subject was reviewed in 1972.[329]

There is some evidence that smoking increases the risk of asbestosis.[315] Another variety of fibrosis (parietal pleural calcification) appears to be strongly associated with industrial exposure to asbestos and to residents in regions where asbestos is produced. Such situations have been reported in Finland from exposure to anthophyllite[314] and in Czechoslovakia from exposure to chrysotile.[330]

Table 5.36. CORRELATION OF INORGANIC FIBERS WITH ASBESTOS BODIES IN LUNGS OF 3,000 CONSECUTIVE AUTOPSIES IN NEW YORK CITY, 1966 TO 1968*

Percentage of cases showing asbestos bodies in relation to occurrence of thin inorganic fibers.

	Thin Inorganic Fibers							
Asbestos Bodies	0		1-4		5-14		15+	
	No.	%	No.	%	No.	%	No.	%
0	1,168	59.5	332	38.3	35	28.0	16	33.3
1-4	705	35.9	424	49.0	52	41.6	13	27.1
5-14	76	3.8	89	10.3	21	16.8	6	12.5
15+	13	0.66	20	2.3	17	13.6	13	27.1
Total	1,962	65.4	865	28.8	125	4.1	48	1.6

Percentage of cases showing thin inorganic fibers in relation to occurrence of asbestos bodies.

	Asbestos Bodies							
Thin Inorganic Fibers	0		1-4		5-14		15+	
	No.	%	No.	%	No.	%	No.	%
0	1,168	75.3	705	59.0	76	39.6	13	20.6
1-4	332	21.4	424	35.5	89	46.3	20	31.7
5-14	35	2.3	52	4.3	21	10.9	17	27.0
15+	16	1.0	13	1.1	6	3.1	13	20.6
Total	1,551	51.7	1,194	39.8	192	6.4	63	2.1

*Correlation was done by optical microscopic study, from Langer et al.[13]

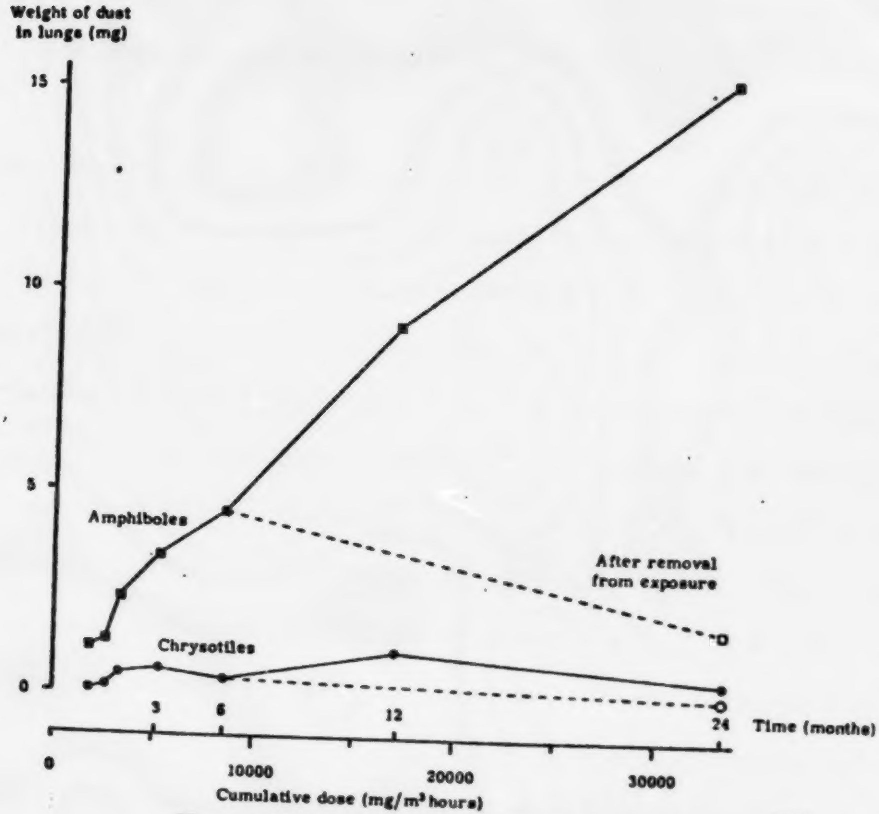
Table 5.37. CHRYSOTILE IN 28 CASES STUDIED BY ELECTRON MICROSCOPY

Group	No. of Chrysotile Fibers + Fibrils	Cases	Male	Female
1	≤9	4/28	3	1
2	10-50	11/28	5	6
3	51-99	6/28	1	5
4	100-200	4/28	4	0
5	≥201	3/28	3	0
"Blank grids"	≤9	--	--	--

Most types of asbestos are fibrogenic. The exact mechanism of action is unclear at this time. But there is evidence that lysosomal injury is involved.[331] Long fibers stimulate more and quicker fibrosis than short ones,[332] possibly because they are less well phagocytized since transport begins with fibers of 20 μ and increases as the fibers become shorter. Short fibers are engulfed by macrophage, long ones are not.[333]

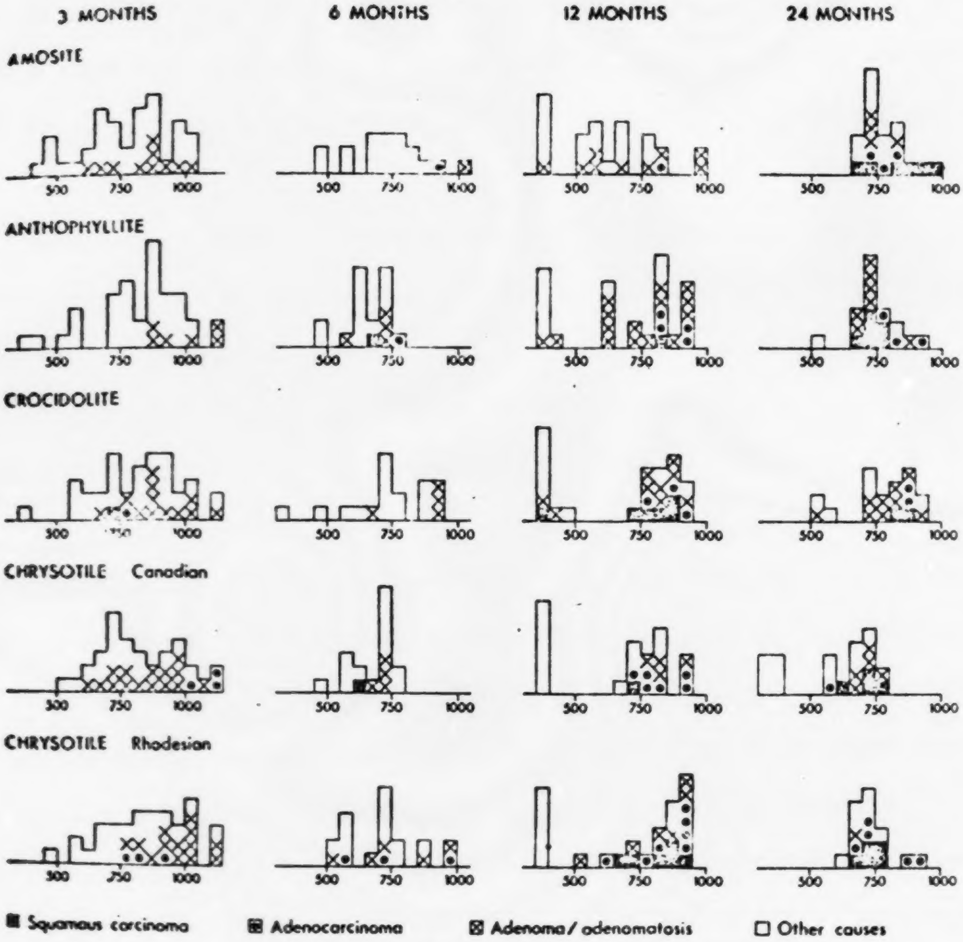
5.1.10.1.2 Pulmonary Carcinogenesis--Exposure of animals by both inhalation and intra-tracheal instillation has produced pulmonary cancer in animals. In one study of rats given chrysotile, one-third of animals surviving 16 months or longer had malignancies of the lung divided about evenly between adenocarcinoma and other tumors consisting of squamous cell carcinoma and fibrosarcoma. One mesothelioma was seen.[324,335] Of interest is the authors' attribution of their tumor yield to concomitant presence of trace metals from grinding methods since they contaminated their asbestos with nickel, cobalt and chromium. But other investigators have produced tumors of the lung and related them to the influence of asbestos alone.

In a recent study of inhalation, S.P.F. rats were exposed to three types of amphibole asbestos (amosite, anthophyllite and crocidolite) and two types of chrysotiles (Canadian and Rhodesian).[326] The rate of deposition and clearance of asbestos dust was studied. Retention was cumulative with length of exposure. When animals were removed from exposure, the amount of dust declined. There appeared to be a better retention of amphibole asbestos (amosite, crocidolite, anthophyllite) than of chrysotiles (Figure 5.6 and 5.7).



—Mean weight of dust in lungs of rats in relation to dose and time.314

Figure 5.6. Effects of inhalation of asbestos in rats



—Distribution of survival times in days after first exposure.

Figure 5.7. Effects of inhalation of asbestos in rats[314]

Tumor induction was found in all forms of asbestos. No tumors occurred until 300 days or more after exposure began. More tumors occurred with 12 months exposure than with six months exposure. But there was no difference between 12 months and two years of exposure. Of interest is the indication in this report that mesothelioma occurs in two amphiboles (amosite and crocidolite) with only one day's exposure to asbestos underscoring potential danger for brief exposure by people.

Tumor frequency relative to treatment is summarized in Table 5.36.

Significant findings in the above study besides successful tumor induction by inhalation routes include: (1) difference in retention rate for amphibole compared to chrysotile and (2) were the approximate equality in the ability of all asbestos tested to induce pulmonary and mesothelial tumors.

5.1.10.1.3 Mesothelial Tumor Induction--Mesothelial tumor induction in experimental animals has been previously mentioned. Mesothelial tumors are readily induced by all forms of asbestos via the inhalation route (see Table 5.38) even though most experiments use intrapleural injection.

A report in 1962 said that crocidolite and chrysotile produced mensothelial tumors in mammals with intrapleural innoculation of the fibers.[336] Since then, many reports have been published on other forms of asbestos and their effects on mice, rats, fowl and hamsters. Experiments suggest that the fibrous nature of the material may have a bearing on the tumorogenicity and a hypothesis could be advanced that carcinogenicity of the material is realated to the ability of its fibers to react with cell membranes without destroying the cells. Also, the presence of trace metals or organics on fibers were not determinates. Particle size and a relationship between the smallness of the fiber and the number of mesotheliomas was more obvious.[320,321]

Other experiments promoted tumors (sarcomas) of mesothelial tissues through use of non-asbestos fibers such as fiber glass and aluminum oxide (AL_2O_3) when placed on a fiberglass mesh and implanted on the pleural surfaces of rats. On the basis of this work, the theory was advanced that a particular configuration of the crystal or fiber was the determinant for tumorogenesis, i.e., diameters of 5 μm or less and lengths of 20 μm or more. However, other studies made with Canadian chrysotile having extremely small fibers produced many mesotheliomas in rats.[320]

But the significance of these reports is somewhat in question because the tumors induced were sarcomas rather than classical mesotheliomas that are tumors of mesenchymal and epithelial characteristics. The histogenesis of pleural and peritoneal tumors is complex. The earliest neo-plastic response often consists of small pedunculated nodules with a central core of reticulin surrounded by a surface of non-differentiate connective tissue. These may spread diffusely over the mesothelial surface as a sheet of connective tissue cells with epithelial cells on the surface. It is assumed that these tumors come from undifferentiated mesenchymal cells in the submesothelial tissue that become differentiated, giving rise to epithelial cells on the surface and spindle-shaped connective tissue cells in the depths.[325]

5.1.10.1.4 Intratracheal Studies--Intra-tracheal studies have been promoted as a convenient method to test the potential of a chemical to

Table 5.38. NUMBER OF ANIMALS WITH LUNG TUMOURS OR MESOTHELIOMATA

Exposure	No. of rats at risk*	No. with lung tumour	Type of lung tumour				No. with meso-thelioma
			Adenoma	Adenomatosis	Adeno-carcinoma+	Squamous carcinoma+	
Amosite							
1 day	45	3	3	0	0	0	1
3 months	37	10	7	3	0	0	0
6 months	18	2	1	0	1	0	0
12 months	25	10	5	4	1	0	0
24 months	21	13	3	1	3	6	0
Total	146	38	19	8	5	6	1
Anthophyllite							
1 day	44	2	2	0	0	0	0
3 months	37	6	6	0	0	0	0
6 months	18	6	3	1	1	1	0
12 months	28	20	9	6	4 (1)	1	1
24 months	18	16	2	5	3	6	1
Total	145	50	22	12	8 (1)	8	2
Crocidolite							
1 day	43	6	5	0	1	0	1
3 months	36	14	10	2	1	1 (1)	1
6 months	18	4	2	2	0	0	0
12 months	26	18	5	4	3	6	2
24 months	18	13	4	5	2 (1)	2 (1)	0
Total	141	55	26	13	7 (1)	9 (2)	4
Chrysotile (Canadian)							
1 day	42	1	0	0	1 (1)	0	0
3 months	34	18	15	0	3	0	0
6 months	17	5	2	2	0	1	0
12 months	23	11	1	3	6 (1)	1 (1)	3
24 months	21	10	2	3	1 (1)	4 (2)	1
Total	137	45	20	8	11 (3)	6 (3)	4

Table 5.38 (continued)

Chrysotile (Rhodesian)							
1 day	45	5	4	0	1	0	0
3 months	36	16	11	2	3 (1)	0	0
6 months	19	8	2	3	3 (1)	0	0
12 months	27	19	2	4	7 (2)	6 (4)	0
24 months	17	11	0	1	5 (2)	5	0
Total	144	59	19	10	19 (6)	11 (4)	0
Control							
1 day	44	4	4	0	0	0	0
3 months	40	3	3	0	0	0	0
6-24 months	42	0	0	0	0	0	0
Total	126	7	7	0	0	0	0

*Rats which survived at least 300 days after start of exposure.
+Numbers in brackets are those with metastases.

induce pulmonary neoplasms and, in particular, to show response to a co-factor in conjunction with a chemical carcinogen. Comparative studies were made using chrysotile and intratrachel inhalation and intrapleural injection.[337]

Intra-tracheal Injection gives a dose-response according to the frequency of injections. The induction of BaP was required to elicit tumors. (Twenty-nine percent of the rats had tumors.)

Inhalation for 13.5 months on a schedule of two hours a day, five days a week, at 230 mg/m^3 produced pre-cancerous lesions in 20% of the rats on chrysotile alone, 59% with BaP added and 38% with tobacco smoke added. A total of 29% of the rats had tumors. Carcinoma of the lungs occurred only in the chrysotile BaP group. Previous experiments demonstrated a slowing of the excretion of BaP with asbestos.[338]

Intrapleural Administration was done by injection of chrysotile three times per month into the right pleural cavity (20 mg fibers in 0.5 ml saline). Almost all the rats experienced local proliferation of the mesothelium that was presumably pre-neoplastic. Mesothelioma appeared after eight months and increased with time: 13 of 47 rats at 8-17 months and 15 of 21 between 18 and 24 months. Forty-six percent of all rats showed mesotheliomas.

As mentioned previously, qualitative differences in fiber size and shape appear to determine induction of mesotheliomas. Carcinogenesis appears to be unrelated to trace metal content or presence of organic matter on fibers. The possible induction of tumors by material other than commercial asbestos has also been considered. And experimental data suggest that a number of inorganic chrystals below 5 μm in diameter may be equally effective in inducing these tumors. The implication of these findings that small, fine particles are the effective component for these tumors is important for industrial and community air pollution control.

5.1.10.1.5 Synergistic Effects--Reference has been made earlier to the remarkable association of asbestos and smoking in promoting bronchiogenic carcinoma in exposed workers in the asbestos industry. Animal exposure by inhalation to chrysotile for 16 months has produced up to 33% pulmonary tumor adenocarcinomos, fibro-sarcomas, squamous cell carcinoma and one mesothelioma.[334] The carcinogens responsible for these were thought to be contaminated by metallic substances from hammer milling.

The same author reported similar findings in a second inhalation experiment.[335] The role of BaP in promoting lung tumors with exposure of animals to various forms of asbestos is known. But the evidence for such effect is at present mainly for chrystotile.[337,338] The other forms of asbestos have not been sufficiently studied in connection with lung tumors.[333]

Contamination by organics including polycyctic hydrocarbons because of geological and industrial factors has also been suggested as a causative factor in pulmonary carcinoma. But the use of fibers after extensive extraction and purification of the material have shown no difference in this regard.[339]

Evidence now available suggests that either: (1) some direct action of the asbestos fiber or interaction with naturally occurring co-factors is responsible for tumorigenesis of the lung in experimental exposure of animals; (2) the addition of BaP or tobacco smoke enhances tumorigenesis with chrystotile; or (3) all forms of commercial asbestos are more or less equally carcinogenic.

5.1.10.1.6 In-Vitro Effects--Much about the basic biological effect of asbestos can be learned from studies in vitro. This work has been reviewed in detail in reference[333] and will only be briefly summarized here.

Among actions reported for asbestos are many similar to silica. These may be listed as follows:

(1.) Lysis of erythrocytes.

(2.) Cytotoxicity on pulmonary macrophages.

(3.) Stimulation of collagen synthesis.

The mechanisms involved are known in many cases and this information may eventually have great value for basic understanding of lesions produced by asbestos, asbestos-like minerals and airborne particles in general. However, their detailed consideration is beyond the scope of this report.

5.2 MATERIALS

5.2.1 Nitrogen Oxide

The damaging effects of atmospheric nitrogen oxides on materials are mainly of concern to the textile industry. Nitrogen dioxide (NO_2) is the troublesome pollutant; nitric oxide (NO) appears to be harmless.

Atmospheric NO_2 can react with a number of important textile dyes and produce noticeable color change or fading. This fading problem has been a problem for the textile industry for decades. A more recent problem concerns yellow discoloration of un-dyed-white and pastel-colored fabrics. Chemists have traced this yellowing to the action of NO_2 on certain additives applied to fabrics to enhance their marketing properties. In the United States, annual gross damage to materials by NO_2 is estimated to be three-quarters-of-a-billion dollars.

These cause-effect relationships have been recognized for years. What is lacking, however, is comprehensive dose-response information. Such information would help to set secondary air quality standards and make cost-benefit studies.

5.2.1.1 Field Studies--Sixty-seven dye-fabric combinations were exposed to different types of urban and rural environments with no sunlight involved. Fading was observed in 43 fabrics. The magnitude of fading was greater in urban areas than in corresponding rural areas, but varied among urban areas. It was impossible to specifically attribute fading to NO_2 since fading might have been caused by other pollutants as well. However, NO_2 was a significant factor for seven of the fabrics.[340]

5.2.1.2 Laboratory Studies--Controlled environment (no light) chamber studies were conducted to assess individual effects of SO_2, NO_2 and ozone on 20 selected dye-fabric combinations. NO_2 was the most potent pollutant, producing the greatest amount of fading on 13 fabrics. Relative humidity was a significant factor in accelerating fading.[341]

Three randomly selected drapery fabrics were exposed to controlled environments (with simulated sunlight) containing three pollutants (SO_2, NO_2 and ozone). Direct and interaction effects of NO_2 caused significant fading in one of the fabrics. A relationship was developed expressing the amount of fading as a function of time, NO_2 concentration and moisture content of the air. A relationship also was developed for the percentage life lost as a function of NO_2 concentration and moisture content of the air.[334]

Exposures in a controlled environment chamber showed that NO_2 had no damaging effect on weathering steel, galvanized (zinc coated) steel, stressed high-strength aluminum alloy, oil base house paint, acrylic or vinyl coil coatings, rubber tire sidewalls, marble and concrete.[3]

5.2.2 Sulfur Dioxide (SO_2)

SO_2 accelerates the deterioration of a wide variety of materials as has been recognized for many decades. Both field and laboratory studies have shown that SO_2-polluted environments (1) increase corrosion rates of most metals, especially iron, steel and zinc; (2) damage a number of building materials such as limestone, marble, roofing slate and mortar; (3) discolor and physically deteriorate statuary and other works of art; (4) increase the erosion rates of oil-base paints; (5) degrade textile fibers, especially cotton and nylon and fade dyed fabrics; (6) embrittle and discolor paper and (7) weaken leather.

Although these cause-effect relationships are well known, the important need today is for comprehensive information on dose-response relationships. Such information is necessary to set secondary air-quality standards and for economists to make cost-benefit studies.

With this in mind, EPA has conducted both field and laboratory studies. The laboratory studies have included controlled environment exposures using specially designed chambers that were scheduled to be used in FY-75 to develop dose-response relationships for economically vulnerable meterials.

5.2.2.1 Field Studies--Ambient levels of airborne SO_2 were major factors in control of rates of corrosion for zinc (galvanized steel). A simple linear function of average SO_2 concentration and averaged relative humidity account for 92% of the variability in average zinc corrosion rates. The useful life of galvanized steel at various average annual SO_2 concentrations and relative humidities can be predicted.[342]

Ambient levels of airborne SO_2 were a major factor in accelerating corrosion rates for steel. Equations were developed for four types of steel relating depth of corrosion to mean SO_2 levels and other factors.[343,344]

Paints containing calcium carbonate extender pigments were found to be particularly susceptible to attack by SO_2 environments.[345]

5.2.2.2 Laboratory Studies--Direct and interaction effects of airborne SO_2 accelerate corrosion rates of weathering steel, galvanized (zinc coated) steel, stressed high strength aluminum alloy and erosion rates of oil-base house paints.[346] Preliminary damage-predictive equations were developed for weathering steel, galvanized steel, stressed aluminum alloy and oil-base house paint, based on laboratory data and known physical and chemical relationships.[346]

Airborne SO_2 does not damage acrylic or vinyl coil (factory applied) coatings, weaken rayon sidewall reinforcing cord in radial rubber tires or produce fading in three randomly selected drapery fabrics.[346]

The effects of airborne SO_2 on marble, latex house paint and concrete were inconclusive.[346]

5.2.3 Ozone (O_3)

Damage by atmospheric ozone occurs mainly to two classes of materials: elastomers and textile dyes. Not all elastomers, however, are subject to ozone damage. Synthetic elastomers with saturated chemical structures have inherent ozone resistance. These elastomers are relatively expensive and account for only a fraction of the market. The great bulk of the elastomers, including natural rubber and synthetic polymers of styrere-butadiene, polybutadiene and polyisoprene, contain double bonds that are prone to oxidation and therefore sensitive to ozone attack.

Researchers have developed anti-ozonant additives capable of protecting elastomers from ozone attack. The protection, however, is not permanent. But for certain items, such as tires, it usually last for the life of the item.

Some important textile dyes fade when exposed to ozone. Certain blue dyes used on acetate and polyester/cotton fabrics and nylon carpets have been particularly troublesome. To prevent or mitigate fading by ozone, the textile industry must use more resistant dyes and/or inhibitors. But these increase the cost of finished goods.

5.2.3.1 Field Studies--Sixty-seven dye-fabric combinations were exposed to different types of urban and rural environments in the absence of sunlight. Two-thirds of the fabrics showed appreciable fading. The fabrics generally faded significantly more at urban sites than at corresponding rural sites. Apparently, air pollutants were responsible for the observed fading. It was impossible, however, to separate the effects of individual pollutants because they were mixed with effects of other pollutants.[347]

A number of paint types were exposed to different environments. Oil-base house paint was the most sensitive. The high smog environment of Los Angeles produced the most damage. It was not possible, however, to identify what pollutant or combination of pollutants was responsible.

5.2.3.2 Laboratory Studies--In controlled environment (no light) chamber studies, low ozone levels (0.05 ppm) produced visible fading in half of 20 dye-fabric combinations and high ozone levels (0.5 ppm) in two-thirds of the fabrics.[348]

In controlled environment (including simulated sunlight) chamber studies of different types of paint, high ozone levels (1.0 ppm) damaged oil-base house paint, but low ozone levels (0.1 ppm) did not.

In more sophisticated environmental (including simulated sunlight) chamber studies of different types of paint, ozone levels up to 0.5 ppm did not significantly damage any of the paint types. Ozone produced small cracks in rubber tire sidewalls. But their rate of penetration was not enough to significantly reduce the life of the tire.[349]

5.3 WEATHER, VISIBILITY AND CLIMATE

5.3.1 Air Qualtiy Trends Analysis

The importance of meteorology in interpretation of trends has been recognized in the first annual report of EPA's Monitoring and Data Analysis Division. An a-typical pattern of significant upward trends in total suspended particulate (TSP) was found over the Western U.S. for 1968-71. This trend is apparently related to a decrease in rainfall over the same period.

TSP monitors are affected by contributions of particulate matter from all sources, including natural dustiness. There appears to be an increase in fugitive dust emission (i.e., agricultural, upward roads, construction, etc.) during drier periods.

5.3.2 Atmospheric Turbidity

Turbidity observations are made only when the line of sight to the sun is free of cloud. The measuring instrument used is called a sunphotometer. It is designed to measure the amount of light received at wavelengths practically unaffected by water vapor absorption. Measurements are regularly made at 80 stations, 50 of which are in the United States.

The Meteorology Laboratory provides the necessary number of instruments and periodically recalibrates them. Although the longest turbidity record is only from 1961, it appears that certain urban areas (Youngstown and New York City) may have atmospheres that are less turbid now than in the mid-60's. The opposite trend may be occurring in some rural areas.

5.3.3 Visibility

Reduction in visibility because of air pollution is, in most cases, caused by scattering and absorption by aerosols. Major progress has been made in development of techniques to determine light scattering and light absorption and to relate these parameters to meteorological range and prevailing visibility or visual range.[350]

Light scattering, as measured by the integrating nephelometer, is highly correlated with sub-micron aerosol volume measured by in-situ techniques and reasonably well-correlated with sub-micron and total aerosol mass. Extensive tests in three California cities of relationships between prevailing visibility, light scattering and aerosol mass concentration indicate that light scattering, as measured by the integrating nephelometer, is a good predictor of prevailing visibility.[351]

Progress has been made in determining the contribution of various aerosol sources to visibility reduction. Because of their hygroscopic or deliquescent nature, secondary aerosols such as $(NH_4)_2SO_4$, NH_4HSO_4, NH_4NO_3 and oxidized organic compounds grow as the relative humidity increases and cause more visibility reduction than their dry weight indicates.[352]

5.4 ECOLOGICAL

5.4.1 Introduction

The over all effect of man's activities on terrestrial vegetation and ecosystems and cumulative effects of his activities on estuaries, coastal areas and the biology of oceans are major ecological concerns. Studies dealing with effects of toxic substances in the biosphere have generally focused on toxic substance effects on individual plants and animals rather than total ecosystems.

The studies usually deal with specific pollutants rather than interactions between and among pollutants. This approach is used with the hope that effective control of specific pollutants and determination of costs of controlling them would be possible, particularly in agriculture. This approach is also used because it is more difficult despite its importance to determine the impact of pollutants on ecosystems in particular and the biosphere in general.

Dr. G. M. Woodwell,[353] however, has shown that disturbances to natural (i.e., non-anthropogenic) ecosystems from any cause produce changes that are similar and predictable. The parameters most changed by pollution are diversity, structure and ratio of photosynthesis to repiration.

Pollution first affects an ecosystem by changing its diversity. Sensitive flora and fauna are eliminated. This results in shorter food chains, fewer symbiotic relationships and less stability. The species affected are those with low reproductive rates, carnivores at the top of food chains and species with the most complex life cycles.[353]

The structure of an ecosystem is affected next. The trend is toward plants of lesser stature. Taller plants are eliminated first. Trees are replaced by shrubs, shrubs by herbs, herbs by low-growing plants and in some instances by mosses and lichens.

The ratio of photosynthesis to respiration is involved in structural change. Chronic disturbance often damages the capability of plants to carry on photosynthesis while not appreciably reducing the total amount of respiration. That makes plants use more energy than they produce. Large plants with large respiration requirements are more vulnerable than small plants.[353]

A reduction in nutrients is also a result of structural change in an ecosystem. A pool of nutrients is released by the decay of larger plants. These nutrients cannot be retained in the soil or recycled. They are lost to aquatic ecosystems where they promote cultural eutrophication of rivers and lakes. This process also points out the link between terrestrial and aquatic ecosystems.[354]

Crop agriculture involves complete replacement of a natural ecosystem with a highly simplified ecosystem composed of plants and animals wholly dependent on care and protection by people and requiring energy inputs. Historically, the continuing development of agriculture has decreased diversity and increased artificiality.

Since World War II, traditional farming with small fields growing a variety of crops and interspersed with pasture and hedgerows or fencerows has been replaced by monocultural systems that are highly vulnerable to pollution, pests and diseases because of low genetic diversity.[355]

Standards set for various substances are based primarily on effects these pollutants have on man and man-made ecosystems. But this is only one aspect of the pollution problem. Not considered is the threat to maintenance of a biosphere suitable for life as we know it. And it does not underscore man's dependence of the integrity of diverse earth ecosystems: those living systems that probably built and now maintain the biosphere.

While toxic substances that are mutagenic to man, either through inhalation or through the food chain, are of great importance, those pollutants that affect components of earth's biota other than man present a greater problem. Effects of pollutants are often chronic and cumulative over time rather than short-lived. And the effects such pollutants have on structure, biological diversity and mineral cycling in ecosystems is not known.[353]

Standards that were set have only superficially attempted to assess effects of those levels on ecosystems. In addition, they have only dealt with pollutant interactions in a cursory way. Little is known about effects of pollutant interactions except for substances involved in photochemical oxidant formation and with nitrogen oxides, ozone and hydrocarbons.[356]

The National Primary and Secondary Standards are the same except for sulfur oxides and particulate matter.

5.4.1.1 Carbon Monoxide--The effects of carbon monoxide in the soil and in aquatic ecosystems still need clarification. Inman et al.[357] found that soil takes up CO in large quantities. But the changes brought about in soil by CO up-take by microorganisms and subsequent production of methane have only been touched upon.[358]

Plants in general are relatively insensitive to carbon monoxide at low concentrations toxic to animals.

5.4.1.2 Nitrogen Oxides--The primary importance of nitrogen oxides involves their participation in photochemical reactions with formation of peroxyacyl nitrates (PAN). The photochemical reactions that produce oxidants have not yet been thoroughly examined.[359]

Evidence of damage to plants from direct exposure to NO_x in the atmosphere is usually confined to the proximity of specific industrial sources. For example, damage from high ambient levels of nitrogen dioxide (NO_2) are observed near nitric acid plants. Direct damage by nitric oxide (NO) and other NO_x components or derivatives have not been delineated in the field because effects on vegetation from the oxides of nitrogen *per se* are difficult to assess.[359]

Most research delineating the effects of NO_x on vegetation was done in the laboratory.[359]

The biochemical-enzymatic mechanisms by which oxides of nitrogen directly injure plants is not understood.[361]

No attempts have been made to determine effect of nitrogen oxide emissions in formation of acid rainfall.

5.4.1.3 Photochemical Oxidants--Photochemical oxidants are products of sunlight-initiated chemical reactions in the atmosphere that involve hydrocarbons and oxides of nitrogen. Those that have been measured in the atmosphere include ozone, peroxyacyl nitrates and nitrogen dioxide. The foregoing shows that photochemical oxidants are a variable mixture of compounds. Each component of this mixture may have a different degree of phytotoxicity so that the composition of the mixture determines the extent of the hazard.[356]

Concentration of total oxidants may vary during the day. While the one-hour maximum may not be exceeded, chronic injury to vegetation may occur because of long-term average concentrations.

The presence of other pollutants and changes in environmental conditions may affect tolerance of plants to photochemical oxidants.[356]

Little is known about the tolerance of plants under field conditions. Selection of a genetically uniform susceptible crop and planting it over large areas could end in large crop losses.[356]

Studies are currently under way to determine effects of photochemical oxidants on the San Fernardino Forest ecosystem.[360]

The primary standard of 160 $\mu g/m^3$ (0.08 ppm) for a one-hour average may not protect all vegetation from adverse effects. A secondary standard should recognize that both concentrations and duration of exposure are important in determining effects on vegetation and ecosystems. Various factors, e.g., soil and humidity, that affect plant sensitivity have not been well-documented.

5.4.1.4 Hydrocarbons--Ethylene is the chief hydrocarbon gas that produces adverse effects at known ambient concentrations. Plants are more sensitive to ethylene than to other hydrocarbon gases.[361] Acetylene, propylene and vinyl chloride all cause phyto-toxicity symptoms resembling those of ethylene. But 60 to 500 times the ethylene concentration is required to produce comparable effects. Ranking according to toxicity is: ethylene>acetylene>propylene>vinyl chloride.[362]

The effects of poly-nuclear aromatic hydrocarbons on higher plants have not been adequately assessed. There is some indication that the aromatic hydrocarbons act as plant hormones.[363]

Studies have shown that gaseous hydrocarbons can be metabolized by micro-organisms.[361] High traffic areas with high amounts of auto exhaust have a soil microflora different from that in low traffic areas. Studies have also shown that natural gas leaking into the soil, because of its utilization by micro-organisms, can stimulate growth in that soil. Gaseous hydrocarbons, then, can affect soil fertility.[364]

Effects of these changes on the growth of higher plants and ecosystems in general have not been assessed. In addition, the effects of hydrocarbons on the microflora of plant surfaces have not been assessed. Changes in microflora of leaf, bark or stem could increase disease susceptibility.

Reactions between atmospheric hydrocarbons and sulfur oxides have not been adequately assessed.

5.4.1.5 Sulfur Oxides--The Secondary Standard of 60 $\mu g/m^3$ (0.1 ppm) annual arithmetic mean and the 24-hour guideline of 260 $\mu g/m^3$ (0.10 ppm) for a 24-hour average were withdrawn in September, 1973. The present standard of 1300 $\mu g/m^3$ (0.5 ppm) for a three-hour average may not protect all vegetation against adverse effects as the standard is close to exposure levels that pose a risk of detrimental economic effects and discernible aesthetic injury to susceptible species of plants.[356]

Chronic effects of sulfur dioxide and their interaction with other pollutants such as ozone, nitrogen oxides and hydrocarbons require further study to consider for the standard. Since environmental conditions not only affect the susceptibility of plants, but effect their distribution, standards that are adequate for one geographic region may not be adequate for another.[356]

The present standard is probably not adequate to control long-term low-level exposure to sulfur dioxide, particularly as it relates to chronic toxicity of sulfate accumulation in plant foliage. The annual average was an index of the concentration of sulfur dioxide and the fraction of time that any measurable concentration was present.[356]

Of increasing concern, but not dealt with by the standards, is the role of sulfur dioxide in acidic precipitation. Long-term average annual concentrations play an important role in the nature and severity of this problem.[356]

The role of sulfur dioxide in changing the pH of plant surfaces has not been studied in the U.S. Studies in Sweden have indicated reduction in growth of pine and spruce trees in areas of high SO_2 emissions. The increased susceptibility to disease of plants so affected or the role of SO_2 in changing ecosystem structure[365] have not been studied to any extent.

5.4.1.6 Sulfates/Sulfuric Acid Aerosols--The sulfates that affect vegetation are formed by chemical reactivity of SO_2 as far as is known. Sulfur dioxide reacting with moisture on the leaf, bark or stem surfaces produces sulfuric acid and causes leaf damage and pH change in the bark. Sulfuric acid mist, acid aerosols, acid rain or sulfate-bearing particulates that dissolve in the dew produce similar effects.[366]

Sulfates are usually considered beneficial to soil and soil organisms except in those cases where they are attached to specific metallic ions. Changes in soil pH because of acidic precipitation may result in soil reactions detrimental to plants and soil-living decomposer organisms. Soils that are acidic or poorly buffered are particularly susceptible.

Sulfate that contributes to formation of acid rain is usually attributed to SO_2 in the atmosphere. The interaction of SO_2 and nitrogen oxides, however, may also be involved.[366]

Studies by Likens, Borman and their co-workers deal with effects of acid rainfall on deciduous forest ecosystems.[367] Neither nitrogen oxide nor sulfur oxide standards have dealt with this problem.

Much overlap exists between the effects of SO_2 and sulfates.

5.4.1.7 Nitrates--The movement of nitrogen through the atmosphere uses three separate cycles: the N_2O cycle, the NH_3 cycle, the NH_3 cycle and the NO_x cycle. The NO_x (nitrogen oxides) cycle has the greatest effect on plant communities and accordingly, other organisms that reside in these communities.[368]

NO and NO_2 from urban sources may move into the atmosphere where reactions with O_3 and water produce HNO_3 vapor and eventually nitrate-salt aerosols. Rain or dry particulate deposition eventually brings nitrate down to the earth's surface. Robinson and Robbins[368] estimate that the amount of nitrates brought down is 462×10^6 tons per year.

The greatest amount of nitrate fallout occurs over oceans. Nitrate fallout of the above-mentioned type has not been directly associated with increasing acidity of rainfall in the Northwestern United States.[367]

The most significant and widespread effects of nitrogen oxides are indirect effects that occur because of involvement of nitrogen oxides in the formation of photochemical oxidants. The nitrogen oxides from combustion processes may enter into photochemical reactions and form peroxyacyl nitrates instead of moving off into the atmosphere in urban areas. The formation of these compounds is discussed in greater detail in the publication, "Air Quality Criteria for Photochemical Oxidants."[369]

The nitrogen oxide standard should help cut down formation of NO_2 and subsequent formation of nitrate aerosols through oxidation. But reduction of atmospheric nitrates will not influence the problem of terrestrial nitrate runoff and euthrophication that results from excess fertilizer application and barnyard runoff.

5.4.1.8 Beryllium--Beryllium, like many trace elements, produces a varied reaction in plants. Both beneficial and detrimental effects of beryllium on plant growth processes have been reported.[370]

Studies show that be-yllium in the soil can be taken in and accumulated by plant roots. Severe stunting of bush beans resulted when they were grown in nutrient concentrations of 0.5, 1.0, 2.0, 3.0 or 5.0 ppm. Abnormal symptoms were progressively more severe as beryllium concentrations increased.[370]

Injury to higher plants from beryllium might occur if high levels of beryllium were dispersed in soil or ground water where plant roots could make contact. Beryllium does not seem to inhibit formation and functions of chlorophyll.[370]

The present standard that prevents emission of high levels of beryllium should be adequate for protecting plants.

5.4.1.9 Mercury--In the Federal Register, Vol. 38, No. 66 - Friday, April 6, 1973 p. 8825, the following statement is made: "Current data on the environmental transport of mercury do not permit clear assessment of the effect of mercury emissions into the atmosphere on the mercury content in the aquatic and terrestrial environments." This statement still holds true. The standard set was intended to protect people from effects of inhaled mercury.

5.4.1.10 Asbestos--Exposure of wild animals to asbestos is not likely unless they are in the vicinity of a man-made source. Then, the standards that protect man should protect them.

Damage to plants is not likely unless the leaves of plants become coated with asbestos to the point where photosynthesis cannot occur.

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6. CONTROL TECHNOLOGY

6.1 STATIONARY SOURCES VS. POLLUTANTS

Stationary combustion sources contribute more to ambient atmospheric loading of SO_x, NO_x and total suspended particulates (TSP) than any other anthropogenic source category. These sources are responsible for (1) approximately 80% of the SO_x emissions, 50% of the NO_x emissions and (2) over 50% of ambient fine particulates.

Industrial processes and open sources (e.g., open burning, mining, incineration, fugitive emissions) are responsible for (1) approximately 16% of the SO_x emissions, 44% of the hydrocarbon emissions, 22% of the CO emissions and (2) over 25% of ambient fine particulates. They are also responsible for most of the hazardous air pollutant emissions (i.e., asbestos, beryllium and mercury), vinyl chloride and other potentially hazardous carcinogenic pollutants.

6.1.1 Particulate Control

The most pressing need in particulate control technology is for development of commercially available and widely applicable fine particle (less than 3 microns) control technology to support the establishment of Fine Particulate standards to provide control of secondary particulate precursors, catalysts and hazardous trace elements. Such technology is inadequate and only just undergoing development under EPA sponsorship.

Scrubbers, electrostatic precipitators and fabric-filter particle collectors are principal particulate collection devices. They are being upgraded by projects concerned with decreasing costs, increasing applicability of devices to a wider range of sources and extending their range of particle collection capability to smaller particle sizes. In addition, entirely new concepts of particle collection are being investigated.

System studies have been completed for each of the conventional devices. These define potential areas of improvement and new applications. Long-range projects include development of generalized models for existing collectors, indentification and laboratory scale testing of totally new concepts in particle control technology and pioneering work in small-particle detection and small-particle generation equipment.

6.1.2 Sulfur Oxides Control

For Sulfur oxides control, achievement of Ambient Air Quality Standards require control of industrial combustion, industrial processes and area sources, including utility combustion. There is only enough natural low-sulfur fuels to satisfy about 40% of the demand of State Implementation Plans. The remainder must be supplied by control technology in the form of effluent desulfurization, fuel cleaning or process modification.

Although the currently defined sulfur oxides control technology program contains developmental projects of sufficient diversity to ensure achievement of Ambient Air Quality Standards, a substantial EPA research and development investment will be required to bring this technology to commercial fruition. Only in the case of effluent desulfurization technology for electric utility applications should control technology achieve widespread commercialization the next few years.

The program has emphasized stack-gas cleaning systems with five or six such processes to be demonstrated before 1976. It has also included work in such areas as fuel modification and desulfurization, industrial process modification and advanced combustion processes.

Most of EPA's early coal de-sulfurization work involved improving and evaluating physical cleaning methods for coal. With the over all potential of physical de-sulfurization and de-ashing of coal reasonably well established, this approach should have moderate applicability in reducing sulfur by 30 to 70% in specific coals. On-going work in this area includes washability testing, coal de-sulfurization and cleaning and pollutant control evaluation and optimization. The most recent work is aimed at chemical de-sulfurization of coal and problems of hazardous pollutants in fossil fuel.

Laboratory-scale technology developments are under way on processes to remove sulfur from coal, producing a clean fuel for combustion. The two processes under development are unique since one is completely selective to inorganic sulfur in coal, the other is being developed for preferential organic sulfur removal and both produce a solid fuel that retains the basic physical characteristics of coal.

The technical feasibility of the inorganic sulfur-removal system has been proven in the laboratory and on the bench scale. It is undergoing scale-up design to a pilot plant size operation. Construction of this plant is scheduled to begin in early 1974. The degree of sulfur removal that can be obtained from the organic sulfur-removal process is currently being quantified in a laboratory apparatus.

This system could be well enough developed by mid-1974 to initiate scale-up design to continuous pilot operation by September, 1974.

The two systems will be examined in detail for their capability for integration into one process scheme for complete removal of sulfur from coal. After successful pilot-plant operation, plans call for scale-up to a demonstration size plant.

Two factors--the major contribution of small coal and oil-burning sources (area sources) to degradation of ambient air quality and the severely limited supplies of low-sulfur fuels--indicate a need for clean fuel or coal conversion processes. CSL has provided funds to both the Bureau of Mines and the Office of Coal Research to assist in development of conversion and gasification processes that can provide clean fuels and to determine what environmental controls will be required for these techniques.

The work on advanced processes primarily involves development of fluidized-bed combustion. Fluidized-bed combustion process options being investigated include: pressurized coal combustion, coal gasification for production of low-sulfur and low-Btu fuel gas and oil gasification. System studies also have been done on development of advanced power cycles.

Work is being conducted to control emissions from smelters, iron and steel operations, refineries, iron foundries, secondary aluminum furnaces and other industrial sources.

6.1.3 Nitrogen Oxides Control

On a national basis, 98% of the nitrogen oxides (NO_x) from stationary sources are from combustion processes. For this reason, the NO_x control program is oriented heavily toward combustion control. Control technologies under investigation to provide near-term solutions to the problem include: combustion modifications such as flue gas recirculation, off-stoichiometric combustion and low excess air operation; identification of alternate or novel combustion systems with inherently low NO_x emission levels; changes in burner design and the use of alternate fuels.

Although flue-gas cleaning processes and advanced power cycles are also being investigated, they may offer longer-term solutions to the problem. Major emphasis in this program has been on coal combustion in utility and industrial boilers since that poses the most difficult problem.

The main approach has been modification of the combustion process to reduce NO_x formation. Bench-scale work and field testing indicate that control for the immediate future can be achieved by this method. In addition, promising stack-gas cleaning processes are being evaluated and investigated on a small scale. Results of this research, however, have not been encouraging so far.

A complicating factor in developing effective control technology is that NO_x are formed during combustion through two separate mechanisms--the fixation of nitrogen in combustion air and the conversion of fuel-bound nitrogen contained in fuels. Although some control of both types of NO_x has been achieved by combustion modifications, it is not known if combustion modification alone will adequately control the NO_x from fuel nitrogen.

6.1.4 Hazardous and Other Control

As EPA regulatory programs develop, the number of pollutants requiring control has expanded to include more than 30 potentially hazardous and annoying air pollutants. Since a majority of the hazardous pollutants are likely to be emitted as particulate matter, there is strong interaction between these two programs.

Examples of specific hazardous and other pollutants under consideration include asbestos, beryllium, cadmium, carbon monoxide, fluorides, hydrocarbons, lead and mercury and odorous materials from rendering plants, pulp mills, sewage treatment plants and chemical process industries. Because of the paucity of data currently available, many problem definition and source characterization studies are required to deal with these pollutants on a rational basis.

6.2 STATIONARY SOURCES VS. CONTROL

Significant advances in development and demonstration of technology to control SO_x, NO_x and primary particulates have already been achieved. Additional improvements in the state of the art are projected for coming years. A brief summary of proven and promising technology under development to control various combustion emissions are described below.

6.2.1 Combustion

6.2.1.1 Fuel Gas De-Sulfurization--Consistent with Congressional guidelines, major concern has focused on control of sulfur oxides from fuel combustion. Expenditures for this have been about 80% of the NERC/RTP Control Systems Laboratory's expenditures to date. And flue-gas desulfurization (FGD) technology development has comprised a major portion of this work.

Flue-gas de-sulfurization systems have been installed on several major commercial power plants in the U.S.A. At least 80 more such systems will be installed by 1980. With the exception of use of clean fuels, flue-gas de-sulfurization is the only sulfur oxides control technology that will have widespread application in the next 15 years. With the expected shortage of clean fuels (amounting to about 20% of the coal demand), flue-gas de-sulfurization will be needed to off-set that shortage.

The need to develop techniques that permit use of eastern and midwestern coal is urgent since only about 7% of this coal is now usable under New Source Performance Standards. And a domestic resource about equivalent in value to the GNP will not be available for use without FGD technology.

Flue-gas de-sulfurization is a technically sound solution that is also economically acceptable. The cost of flue-gas de-sulfurization for coal-fired power plants should be 2 to 3 mills/Kwbr(3) compared to 2 to 4 mills/Kwhr(4) for naturally-occurring clean fuels delivered to the power plant site and even higher costs of approximately 8-13 mills/Kwhr(3) associated with coal gasification technologies.

6.2.1.1.1 Sodium hydroxide scrubbing with electrolytic regeneration (Stone & Webster/Ionics)--In July, 1972, EPA and Wisconsin Electric Power Company (WEPCO) initiated a 3-1/2 year, three-phase program involving the Stone & Webster (SWI) sodium hydroxide scrubbing process.

In Phase I, recently completed, an integrated pilot plant was built. Operating tests were performed for about a one-year period and a prototype-scale electrolytic cell system was designed, fabricated and tested. Preliminary design of a 75 MW prototype system and development of detailed test programs and operating schedules for the prototype system were also completed. The Phase I final report was scheduled for publication in late 1974.

Based on favorable assessment of Phase I results and continued technical and economic viability of the process, a 16-month-long Phase II effort is being considered for the detailed design, procurement and installation of the 75-MW prototype. This would be followed by Phase III, a 12-month start-up and operational period for the 75-MW prototype. Assuming a decision to proceed, EPA and WEPCO would co-fund the $7 million program.

Chief advantages of the process, expected to apply to both existing and new power plants over a broad range of sizes, are: highly efficient removal of SO_x; production of easily handled non-slurry flow streams; no solid waste; and recovery of SO_2 for subsequent processing into liquified SO_2, sulfuric acid or elemental sulfur.

Potential disadvantages of the process include: power requirements for electrolytic regeneration, adverse influence of particulate and flue-gas trace constituents on reliability of the electrolytic cell and need to remove from the system any sulfates produced by oxidation in the scrubber. The Phase I final report will evaluate and assess these potential disadvantages.

6.2.1.1.2 Catalytic oxidation (Monsanto Cat-Ox)--The catalytic oxidation (Cat-Ox) process is an adaptation of the contact sulfuric acid process. Monsanto Enviro-Chem Systems, Inc. has developed this adaptation through work on a pilot-scale unit and a 15-MW prototype. EPA and Illinois Power Company (sharing a $7 million total funding requirement) prepared to demonstrate the process on a 100-MW coal-fired boiler at Illinois Power's Wood River Station by late 1974 with accompanying commencement of the one-year test program.

The Cat-Ox system is available in two configurations: the Reheat system for retrofitting existing plants and the Integrated system for incorporation into new power generating facilities.

The Reheat system operates with flue gases passing first through a high efficiency (99.6%) electrostatic precipitator. Then, in preparation for catalytic conversion of the SO_2 to SO_3, the temperature is raised to about 850°F. This heat is added in three increments by: a primary input from an external combustor, a gas heat exchanger and a secondary input from the external combustor.

After heating, SO_2 contained in flue gases is converted to SO_3 by the catalyst. Leaving the converter, the hot flue gases pass through the high-temperature side of the gas heat-exchanger to the acid production section. The sulfuric acid is formed by the standard SO_3-H_2O absorbing tower contact process.

The acid product is cooled and sent to storage while the flue gases pass through a fiber-packed mist eliminator (where residual traces of sulfuric acid mist are removed) and on to the stack where clean gas exits to the atmosphere. At this point, essentially all particulate matter and 85% of the SO_2 have been removed from the gas stream.

Trace and hazardous element analyses account for an important portion of the over all Cat-Ox test program. A complete characterization of Wood River Unit No. 4 (prior to Cat-Ox equipment tie-in) included analyses for some 30 trace elements in the coal, hopper ash and slag. Other analyses included fly ash, where elemental analysis has been done for a complete range of size fractions. These tests will be repeated during the one-year test program (after the Cat-Ox system becomes operational) to determine effects of the system on concentration and distribution of trace elements.

6.2.1.1.3 Sodium ion scrubbing (Wellman-Lord)--EPA has high confidence for success of this first coal-fired boiler demonstration system in meeting guarantees for pollution control, product quality and material and utility requirements. This confidence is based on the already large amounts of successful operating experience to date for W-L Systems on various applications, including acid plants, Claus plants and oil-fired boilers. Seven systems are now in operation in the U.S. and Japan.

The knowledge gained from operating these systems has produced a series of process improvements (reducing costs and purge requirements) that are incorporated in the EPA/NIPSCO demonstration (115 MW coal-fired power plant for 90-95% SO_2 removal efficiency). CSL is considering expansion of the Wellman Power Gas Demonstration to achieve 98-99% removal efficiency. This could be done with little interruption of the current project and at an incremental cost of approximately $400,000-$2,000,000, depending on the length of the high efficiency trials.

As an on-going project with high efficiency potential, the Wellman Power Gas System (Sodium base scrubbing) could be the first technique available to achieve eventual SO_2-sulfate standards. Data from the Wellman Demonstration could be available prior to 1978.

The SO_2 product from the W-L Process is suitable for recovery in three forms: liquid SO_2, sulfuric acid and elemental sulfur. For purposes of the EPA/NIPSCO demonstration, the Allied Chemical SO_2 Reduction Process will be applied to generate a most salable and environmentally sound product elemental sulfur. The Allied Process uses natural gas as a reductant in a novel catalytic reactor system. The process has been demonstrated on a large scale with treatment of a 12% SO_2 gas stream from a nickel ore roaster at Sudbury, Ontario.

6.2.1.1.4 Citrate process--EPA and the U.S. Bureau of Mines are cooperating and pooling funds and technical talents to demonstrate the Citrate Process developed through pilot scale by the Bureau of Mines. A concurrent development program by an industrial consortium headed by Pfizer Chemical Company also led to a successful pilot operation using the process. Based on the success of these two pilot programs, EPA and the Bureau of Mines decided to demonstrate this technology at the 30 to 60 MW scale.

Current plans call for two separate demonstration plants: one to treat oil-fired flue gas and the other, coal-fired flue gas. Negotiations are currently under way with prospective host sites and process vendors. Contracts were to be signed in the Spring of 1975 for these two projects that will include substantial cost sharing by the host site.

The Citrate Process consists of five steps: gas cleaning and cooling, sulfur dioxide absorption, sulfur precipitation and solution regeneration, sulfur separation and hydrogen sulfide generation. Although a number of reactions take place in the reactors, the net reaction is combining of sulfur dioxide and hydrogen sulfide to form elemental sulfur.

Based on favorable projected economics for the Citrate Process and encouraging results at the Pfizer and Bureau of Mines pilot plants, the process is considered a candidate for commercial application of a second generation flue-gas de-sulfurization process.

6.2.1.1.5 Ammonia scrubbing with bisulfate regeneration--Stack gases have been commercially de-sulfurized with solutions of ammonium sulfite and bisulfite since the mid 1930's. The early processes recovered SO_2 in pure form by acidifying the scrubbing liquor with such acids as sulfuric, nitric and phosphoric. The resulting ammonium salt of the acid was further processed for use as a fertilizer.

Because of the enormous tonnages of SO_2 involved in de-sulfurizing power-plant stack gases, fertilizer markets will not support wide-scale use of fertilizer-producing ammonia processes. So CSL, in a joint venture with TVA, is developing a completely cyclic ammonia scrubbing/bisulfate regeneration process that has a concentrated stream of SO_2 as its major product.

The process (shown below) removes SO_2 from stack gases by absorption in a solution of ammonium sulfite and bisulfite. Scrubber product liquor is acidified with ammonium bisulfate to produce SO_2 and form ammonium sulfate. After condensing out most of the water, a pure stream of SO_2 can be further processed to sulfuric acid, elemental sulfur or liquid SO_2.

Three purge methods can be used. If a fertilizer market exists for ammonium sulfate, ammonium sulfate crystals can be purged prior to decomposition. It there is no fertilizer market, ammonium bisulfate can be reacted with lime to form gypsum and regenerate the ammonia. And ammonium bisulfate can be injected into the utility boiler where it will be decomposed into nitrogen and SO_2.

In 1973, attention focused on eliminating an objectionable plume of ammonia-based salts in scrubbed gas leaving the stack. Based on visual observation, this plume was eliminated or reduced to an acceptable opacity by quenching the flue gas with water prior to introducing the gas into the ammoniacal scrubber. Other explanations can be offered for elimination of the plume, but they are considered less likely.

During FY 74, the pilot plant was modified. A venturi-type prescrubber was added to humidify and cool the incoming gas and remove particulates and chlorides. Two marble-bed stages were replaced with Koch valve trays and another valve tray was added. An evaporator/crystallizer was installed to produce solid ammonium sulfate in the regenerator section. The pilot plant was operated for two periods totalling about four months of operating time.

The pre-scrubber reduced particulates and chlorides by about 93% (average) and essentially 100% respectively. Typical sulfur dioxide removal efficiencies in the scrubber were 90% or greater. Observed plume opacity was about 5% or less and ammonia losses were in the 10-30 ppm range.

CSL's efforts during FY 75 focus on improved sulfur dioxide recovery from rich scrubber liquor, improved scrubber performance through reduction of inter-stage mixing and better control and improved mist elimination. In addition, an electrical decomposer is being designed and fabricated. The decomposer regenerates ammonium bisulfate and ammonia and is expected to be operational early in FY 76, allowing integrated operation of the pilot plant.

6.2.1.1.6 Magnesium oxide (Chemico Mag-Ox) scrubbing--A two-year stack-gas scrubbing demonstration funded by EPA/CSL using a magnesium oxide slurry has been successfully completed on Boston Edison's oil-fired, 155 MW steam electric plant, located at Mystic Station, Massachusetts. The chief advantage of the process is its wide applicability to both existing and new steam-electric plants and its highly efficient removal of both sulfur oxides and particulates with no interference to boiler operation. Sulfur removal efficiencies in excess of 93% have been achieved.

During final months of the demonstration phase, the control system availability approached 90%. This level of availability is significantly better than in previous periods of operation. Removal efficiencies cited above are adequate to meet existing sulfur oxide emission standards. The ability of the process to produce high-quality sulfuric acid for marketing was clearly established.

This control technology is of special importance because it is environmentally clean. There is no disposal of waste products after processing the magnesium oxide slurry for sulfur recovery and marketing and recycling of recoverable magnesium oxide. Industrial support is evidenced by new construction planned by other utility companies implementing this process.

6.2.1.1.7 Activated carbon--The use of multi-stage, dry fluidized beds of recycling activated carbon appears attractive both for sorption of SO_x from flue gases and for converting removed SO_x to elemental sulfur. Under an EPA contract, development of the activated-carbon-based flue-gas de-sulfurization process has advanced to a stage where three major process units--sorber, sulfur generator and carbon regenerator--are integrated for continuous and cyclic operation.

Integrated pilot plant operation, a culminating point in efforts to determine over all technical feasibility of the process, is complete.

Cyclic operation of the approximately 300 scfm capacity pilot plant has produced encouraging preliminary results. Estimated process economics based on such results compare favorably with those of other flue-gas de-sulfurization processes. Westvaco, EPA's contractor, was to provide a detailed final report early in 1975 on this process development.

6.2.1.1.8 Lime/Limestone wet scrubbing--Lime/Limestone scrubbing is the prevalent FGD technology in the U.S. today. Eleven of 16 operational facilities are either lime or limestone scrubbing systems. And 13 of 18 FGD facilities currently (November, 1974) under construction are lime or limestone systems.

In 1972, EPA initiated a program to test a prototype lime and limestone wet-scrubbing system to remove sulfur dioxide and particulates from stack gases. Three scrubbers (10 MW equivalent each) of different design were connected to stack-gas ducting of a coal-fired boiler at the TVA Shawnee Power Station, Paducah, Kentucky. Bechtel Corporation was the major contractor.

Major goals of the program are to: (a) characterize effects of important process variables on sulfur dioxide and particulate removal; (b) develop mathematical models for design of full-scale systems for installation at other power plants; (c) perform long-term reliability testing; and (d) conduct a sludge disposal evaluation program.

Reliability of both the limestone and lime scrubbers has been improved. The scrubbers can be operated continuously for three months before shut-down is required to clean the mist eliminator. Present efforts focus on solving the mist eliminator pluggage problem. That would allow reliable operation for periods of six months and longer.

During system testing, over all particulate removal efficiencies of 98.4 to 99.4% and SO_x removal efficiencies of 77 to 99% were obtained. System tests continue with modification of various operating parameters to determine effects that such changes have on system reliability and system performance.

The sludge disposal evaluation program has recently been initiated. This program will evaluate disposal of both untreated and treated (fixated) lime and limestone sludge materials.

6.2.1.1.9 Double alkali--The double-alkali process, like lime/limestone wet-scrubbing processes, produce a throwaway product consisting of fly ash and calcium sulfite/sulfate. The process was developed in various forms in an effort to avoid problems associated with use of absorbent slurries in lime/limestone processes. The Double Alkali Process uses a clear scrubbing liquor containing soluble alkali species rather than absorbent slurries.

Although less thoroughly researched and developed than lime/limestone wet-scrubbing processes, double-alkali systems have the potential to attain high sulfur-oxide removal efficiency and good reliability at competitive costs. One problem associated with these systems is the potential for ground and surface-water pollution by solubles in the waste product. However, there are ways to reduce or eliminate this potential secondary problem.

6.2.1.2 Combustion modification--Combustion sources contribute about 98% of NO_x emissions from stationary sources. Studies to date indicate that combustion modification is the principal method available in the near future to control NO_x emissions from combustion of fossil fuels.

The most promising combustion modification techniques include combustion with low excess air, recirculation of flue gas in the fuel/air mixture, staged combustion and burner/combustor re-design.

So far, flue gas recirculation has been the most effective combustion control technique for NO_x emission from nitrogen fixation of atmospheric nitrogen. Staged combustion is the most effective control method for NO_x emissions from fuel nitrogen conversion. The development of this technology by EPA has allowed control of NO_x emissions from gas- and oil-fired utility boilers to a level of 150-250 ppm. In short-term testing, combustion modifications have also resulted in NO_x reductions of up to 50% in commercial coal-fired utility boilers.

Also, burner and furnace design variables cause widely varying NO_x emission levels in all boiler categories. Current efforts are directed at continued development and demonstration of modified operating procedures for NO_x control in pilot- and commercial-scale demonstrations of combustion control of NO_x for existing and new combustion sources in all size categories.

In addition, R&D efforts will be extended to develop control technology applicable to combustion of additional fuel types (including coal-derived fuels such as low Btu gas, mixed fuels, waste fuels, mathanol, etc.) and covering a wider range of combustion equipment (e.g., stationary gas turbines, internal combustion engines, industrial process furnaces, etc.).

EPA/CSL has recently completed a field test program to study method of reducing NO_x formation in coal-fired steam generating units. Introduction of biased firing has developed as a product of this study. Under these conditions, fuel-rich first-stage firing is followed by delayed introduction of the total combustion air supply. In actual measurements, the NO_x emission level was 1.04 gms $NO_x/10^6{}_{cal}$ or 17.5% lower than the New Source Performance Standard.

6.2.1.2.1 Utility boilers--

Control Limitations--Although general techniques are well known, results of application of these techniques to practical combustion systems are still uncertain. Most applications to now have been retrofits to existing equipment and they do not approach optimum levels of NO control that should be achieved.

Application of techniques is difficult because they must be applied in a manner that prevents increases of other pollutants (i.e., - CO and smoke) and losses of system efficiencies. Further development work is needed, particularly for heavy oil and coal-fired systems. The impact of various alternate fuels on the control techniques must also be assessed.

Control Application Experience--Implementation of combustion modification techniques to date have been almost exclusively used with utility boilers. The Los Angeles APCD has had standards for existing gas- and oil-fired utility boilers for some time (until December 31, 1974, 225 ppm for gas and 325 ppm for oil). These standards are being met using combinations of staged combustion, low excess air and flue gas recirculation.

In addition, the Los Angeles APCD has a regulation limiting new units, regardless of size, to 140 lbs. per hour. That means that a 315 MW boiler can emit about 40 ppm NO (@ 3% O_2). A unit (Scattergood

3) has been installed that is expected to meet this limit firing natural gas. This unit uses the full range of available combustion modification techniques and if successful, will significantly advance the state of the art of application to gas-fired utility boilers.

Federal standards have been set for new (ordered after August, 1972) utility boilers greater than 25 MW for all fuels. The approximate levels are: 168 ppm NO for natural gas, 230 ppm for oil and 500 ppm for coal (all concentrations are at 3% O_2 dry basis).

Boiler manufacturers are currently selling units guaranteed to meet these standards. Staged combustion, low excess air and burner design changes are being combined to meet these regulations. The main uncertainty is how to achieve the standards on coal wall-fired boilers.

As previously mentioned, combustion modification techniques used to control NO_x may adversely affect emissions of other pollutants (i.e., - CO, HC and particulates) and system efficiency. However, since much of the data from existing field equipment is not designed for application of these techniques, the significance of these adverse effects must be carefully assessed. There is good evidence that a system initially engineered for NO_x control can also achieve emission standards for other pollutants at equal or greater efficiency.

6.2.1.2.2 Industrial/residential/commercial boilers--For other sources--industrial and commercial boilers, residential heaters, industrial process furnaces and stationary internal combustion engines--no standards have been proposed. The R&D for each of these sources is in various stages of progress and will influence both standards and implementation schedules.

The residential and commercial boiler field tests were initiated by Battelle-Columbus Laboratories in October, 1970 under sponsorship of the American Petroleum Institute (API). To expand EPA's in-house studies in this area, a follow-up program jointly sponsored by API and EPA was awarded to Battelle and completed in September, 1973. The tests were primarily with oil-fired equipment, but some gas-fired boilers were included.

The equipment used ranged from 80,000 to about 20,000,000 Btu's per hour. The major conclusion reached was that combustible emissions from residential equipment can be greatly reduced by proper servicing. By replacing old, worn-out units, CO emissions were reduced by more than 65%, HC emissions were reduced by 87%, filterable particulate by 17% and total particulate (filterable and condensable) by 33%. Tuning the burner by proper service methods further reduced CO emissions for a total reduction of more than 81%.

The Bacharach smoke number was reduced by 59%. Even these reductions are conservative since Battelle only included burners that were under a burner service contract. The findings strongly indicate that emissions from residential sources could be reduced to insignificant levels simply by proper maintenance that identifies units in need of replacement and by tuning the remainder. Significant NO_x reductions should result from burner re-design programs described elsewhere in this Report.

The major results from commercial boiler operations were that emissions are mainly affected by boiler and burner design and fuel type. Also, for commercial boilers operating at steady state conditions, Bacharach smoke numbers showed consistent trends in relationship to filterable particulates when firing different oil in the same boiler.

Earlier studies have indicated that the most important source of polycyclic organic matter, particularly benzo(a)pyrene, was inefficient combustion of coal in small hand-fired residential furnaces. At present, a study is under way to evaluate emissions from combustion of coals of various types in a stoker-fired system and to assess combustion of smokeless coal. The ultimate aim of this work is to provide improved low-emission technology for operation of this class of residential and small commercial coal-burning furnaces.

6.2.1.2.3 Gas turbines--Publication of New Source Performance Standards for stationary gas turbines was planned for December, 1974. Standard setting was planned for the first half of 1975. It appears that different standards may be established for gas and oil-fired units. Current target levels for stationary gas turbines of over 1.5 million Btu/hr. (about 125 HP) are 77 ppm NO_x (15% excess oxygen) for oil-fired units and 55 ppm NO_x (15% excess oxygen) for gas-fired units.

Combustion modification experience has centered chiefly on methods to reduce peak temperature. Although interim methods such as water or steam injection and exhaust gas recirculation offer potential for significant reductions in NO_x emissions, advanced combustor concepts will be needed to achieve optimum control of all pollutants. Turbine manufacturers are developing low NO_x combustors since they think that "dry" controls will be more economical and attractive to users. At present EPA is conducting surveys and field tests of gas turbines to establish the state of the art of control technology and to identify R&D requirements for these sources.

6.2.1.3 Primary Particulate Control Devices--Initial work has emphasized characterization of conventional control equipment. Prior to January, 1975, sufficient data should have been available to learn about the actual control capability in terms of fractional efficiency of electrostatic precipitators, fabric filters and wet scrubbers. A series of tests are under way to determine relative collection difficulty associated with specific industrial dusts. Plans to accomplish this call for use of standardized control equipment (pilot scale) with accompanying measurement systems available on mobile mounting. This will facilitate comparison of numerous sources. The standardized equipment include a fabric filter, two scrubbers and an electrostatic precipitator.

In the past year, CSL has been involved in a program designed to find acceptable methods to control emitted fine particulate matter. Program results so far indicate that several conventional devices, such as fabric filters, high efficiency electrostatic precipitators and certain high-energy scrubbers, are able to control fine particulate emissions on particulate matter as small as 0.01 microns in diameter. These devices, to be effective, must be designed, operated and maintained to a very strict standard. Much additional work is necessary to reduce capital and operating costs associated with these devices when they are used as fine particulate control devices.

CSL is conducting field tests of industrial ESP's to determine fine particle collection and economics of ESP systems. Recent results indicate that properly designed and operated ESP's can control fly ash from coal-fired utility boilers at an over all mass efficiency in excess of 99%. These same efficiency measurements indicate that these ESP's are more than 90% efficient on a mass basis in collecting all particle size fractions as small as 0.01 microns.

Last year, full-scale fabric filter systems on combustion sources were characterized as to their ability to remove particulates as small as 0.01 μm. Test results show that the filter systems typically operate at 99.8% over all collection efficiency and at greater than 99% efficiency even for sizes as small as 0.1 μm.

Work is also being done on particulate collection at elevated temperatures and pressures as required to meet the needs of coal-combustor-gas turbines and coal gasification processes. Development has started on high-temperature electrostatic precipitation. Granular filters, special inertial separators and other high temperature devices are being evaluated for particulate clean-up on a fluidized bed coal reactor.

6.2.1.4 Novel Combustion Systems

6.2.1.4.1 Fluid bed combustion--Under contract to EPA/CSL, Exxon R&E is investigating sustained operation parameters of a coal-fired pressurized (10 atmos) 630 KW mini-plant at their Linden, N. J. headquarters. Sustained operation attainment has been delayed for about six weeks to correct minor technical problems.

Significant increases in combustion efficiency and improved pollution control are attainable by fluidized bed combustion. This offers the greatest potential for producing electrical energy from fossil fuels within present environmental constraints and at a lower cost than conventional power plants using low-sulfur fuel or stack gas cleaning.

6.2.1.4.2 Refuse firing for steam generating--A CSL study to evaluate technical aspects, cost effectiveness and environmental benefits of burning municipal refuse in utility grade boilers was completed by the Envirogenics Company in 1971. Cost analyses indicated that, in most cases, solid waste disposal costs would be significantly less than the cost of disposal in a municipal incinerator. In some instances, savings were $2 to $5 per ton of refuse burned. Analyses also indicated that if all available refuse in a selected large metropolis were to replace coal in power plants not currently having SO_2 control, SO_2 burdens in that air pollution region would be reduced by about 7%. There would also be a moderate reduction in atmospheric particulates.

The feasibility of burning shredded municipal wastes as a supplementary fuel in coal-fired utility boilers is being demonstrated in a program sponsored by EPA, the City of St. Louis and the Union Electric Utility Company. A waste processing plant has been constructed and firing facilities have been constructed at a power plant 18 miles away.

Initial tests were conducted by Union Electric of St. Louis, Missouri, to determine effects of combined firing of shredded refuse and coal on pollutants emitted from a boiler, boiler operating characteristics, efficiency of the electrostatic precipitator and combustion efficiency of solid waste as fuel. Tentative conclusions indicated that increased refuse firing rates produce increased combustion efficiencies. No significant changes were noted in gaseous pollutant levels when refuse and coal are fired together under test conditions. However, there is an apparent decrease in electrostatic precipitator efficiency.

This drop in ESP efficiency is probably the result of increased gas flow-rates and changes in ESP operating characteristics. Additional tests are being undertaken to further investigate effects of refuse processing and firing on emissions and energy recovery. Successful completion of this project will help solve solid waste disposal problems and add an increment of fuel to meet industrial needs.

6.2.1.5 Catalytic reduction--In a contract with Environics, Inc., selective noble metal reduction of NO_x with ammonia is being explored on a pilot scale. The experimental system uses a side stream equivalent to 2 MW from a gas-fired utility boiler as a flue-gas source. The flue gas, containing around 225 ppm of NO, is mixed with ammonia and then contacted with a catalyst bed at elevated temperature. NO_x reductions of 90% have been achieved. However, equal or greater amounts of NH_3 (e.g., 25-30 ppm) are also present in the exhaust.

The pilot scale unit has accumulated about 2000 hours of testing with natural gas firing with essentially no performance degradation of the catalyst. Current plans, made necessary by recent natural gas curtailment for utility use in the Los Angeles area, are to test with sulfur-containing flue-gas beginning in the Winter of 1974. In preparation for testing with flue-gas from oil combustion, an electrical pre-heater has been installed to raise flue gas temperature prior to entering the catalyst bed. A report on pilot plant results with gas firing and oil firing should be available in Spring, 1975.

TRW Systems has done a technical and economic assessment of various catalytic schemes for NO_x control for stationary power plants. The purpose was to review catalyst technology for NO_x abatement, assess technical and economic feasibility of various schemes, evaluate applicability to power plants and recommend the most promising schemes. A comprehensive data bank was developed with about 250 articles and patents on pertinent NO_x catalysts and catalytic processes.

On a lab scale with simulated flue-gas (without fly ash), catalytic reduction of NO was investigated over space velocities ranging from 5,000 to 20,000 hr^{-1} STP and at temperatures from 200 to 450°C. Approximately 45 catalysts were screened to determine nonselective NO_x reduction with H_2 and CO and selective reduction with NH_3, H_2 and CO. Identified as being most promising (because of their activity) for selective reduction with NH_3 are iron-chromium, venadium, copper-lead, molybdenum and platinum catalysts.

Parametric investigations of best catalyst systems with major emphasis on selective NO_x - NH_3 non-noble systems have been completed. These parametric studies indicated NO conversions of about 60-95% with NH_3 stoichiometry about 1.0, temperature of 400°C, space velocities of 5000 to 20,000 hr^{-1} and inlet NO concentrations of 250-1000 ppm.

Preliminary capital and operating cost estimates for application of this process on an 800 MW power plant are $6.15/Kw and .88 mills/Kwh respectively. These estimates assumed fly ash removal prior to NO removal and that the SO_x present did not affect the catalyst. This latter assumption was verified in preliminary screening of Fe-Cr and vanadia catalysts.

6.2.1.6 Fuel Cleaning

6.2.1.6.1 Coal--The goal of the coal-cleaning program is to determine the impact that coal cleaning could have on control of sulfur oxide by increasing supplies of low sulfur coal. The approach taken here has been to identify qualities of U.S. coals, potential sulfur reduction attainable by physical methods and improvements in coal-cleaning techniques that would maximize sulfur reduction.

So far, this program has achieved many of its objectives. The vast coal float-sink testing program initiated in 1965 is 75% completed. Evaluations and applicability of existing physical cleaning techniques are complete. And modification of froth-flotation to obtain sulfur reductions not achievable before have been piloted. The emphasis placed on R/D in coal and coal-cleaning programs by EPA has stimulated interest in additional efforts by other organizations.

The work supported at TRW on chemical extraction of pyrite involves an approach that would achieve 95 to 100% pyrite removal. The full development of this approach would enable coal processors to guarantee sulfur reduction to levels that would meet new performance standards.

In the Appalachian coal states (Alabama, Maryland, Ohio, Pennsylvania, Tennessee, Virginia and West Virginia), much of the coal currently mined could be reduced to a 0.75% sulfur level or less by application of the Meyers' process. The combination of mechanical and chemical cleaning techniques would enhance the over all applicability of coal-cleaning technology and should improve coal-cleaning economics.

A shift in production to specific coal beds could make an even more significant impact. The coal-cleaning plant in the near future, then, would most likely involve an integrated physical and chemical removal process that would produce a coal of lowest sulfur and lowest ash with a minimum of trace metallic constituents.

CSL has recommended that a prototype coal cleaning demonstration plant not be built. They think that EPA can have the greatest impact through technical support in engineering systems for coal cleaning (in conjunction with other control techniques where required) that would result in the most appropriate control strategies.

Such an approach has been initiated with the state of Iowa. CSL will provide a technical data base for coal cleaning (mechanical and chemical) and other control methods that will allow for development of strategies to meet Iowa's short- and long-range programs. In this study, it is evident that coal cleaning will not only be an initial technique to meet current state standards, but may be a necessary step to meet long-range sulfur emission levels.

An integrated coal cleaning development program would result in the earliest availability of a process that could have maximum impact on all users of coal. In the Appalachian coal region, use of this combined approach on coals now being mined for combustion purposes would result in 50 to 60% of the coals having a sulfur level less than 0.75% and 70 to 80% of the coals having a sulfur level less than 1.0%. The use of these lower sulfur-level coals could achieve the following results:

1. Residential users (normally the lowest income group) would not have to switch to other fuels. In many cases (such as in Philadelphia, Detroit, Chicago, etc.), this user group could not financially afford to switch from coal to gas or oil.

2. Industrial and commercial users (using about 15% of the combustion tonnage) could meet existing standards and avoid requirements to switch to alternate fuels.

3. Large utility users, in the majority of cases, should be able to meet state standards for existing units and many new or planned stations could use coal instead of gas or oil. The continued use of coals would aid in and prevent increased use of gas and oil by the utility industry.

So over all, there would be an increase in the use of coal by the utility industry and an increase in availability of gas and oil to area source users who have few alternative control strategies available to them.

EPA/CSL is currently negotiating for construction of a chemical coal de-sulfurization pilot plant. This technology will not be available for commercial application until the mid-1980's.

6.2.1.6.2 Liquids--Much of the oil currently available in the U.S. for fuel is high sulfur, high metal content residual oil. Even if these oils could be economically de-sulfurized, high vanadium and nickel content would probably present environmental problems and would certainly cause equipment problems in combined cycle operations. Nitrogen contents of these oils can also be a problem especially with combined cycle operation.

Because of the inter-related and dependent nature of these contaminates, EPA/CSL has programs to study separate and combined effects. For example, both enhancing and inhibiting effects of simultaneous hydro-de-sulfurization and hydro-de-nitrogenation reactions have been observed. Additional discussions of liquid fuel cleaning are presented in the section on Coal Conversion.

6.2.1.7 Fuel Gas Production

6.2.1.7.1 CAFB--The Chemically Active Fluid Bed (CAFB) process for gasifying and de-sulfurizing heavy oil has been demonstrated in a 0.75-MW continuous pilot unit at Esso Research Center, Abingdon, England (Esso, England). The CAFB process involves injection of heavy fuel oil into a shallow (about two feet deep) fluidized bed of lime/limestone particles to partially oxidize, gasify and de-sulfurize the oil. The continuous pilot unit fires a commercial boiler rated at 10 million Btu/hour and demonstrated a service factor of 95% in the latest run of about 400 hours duration.

In addition to 90% sulfur removal at a calcium-to-sulfur feed ratio of 1.5 to 1, the CAFB has completely removed vanadium and has removed 75% of the nickel and 36% of sodium. A reduction in the NO_x emissions from 263 ppm (when the boiler was oil-fired) to 160 ppm (when fired on the CAFB product) has been demonstrated.

Economic studies continue to show that CAFB is a viable commercial process. The effluent from the limestone regenerator is 5-10% SO_2 and can be reduced to sulfur using existing technology. Demonstration of a 50-MW unit is planned at Providence, R. I. New England Electric System (NEES, a private utility) is participating in a process design effort with Stone and Webster Engineering Company (SWEC), Esso England and Westinghouse Research Laboratories, under EPA sponsorship, to design the demonstration unit. The sulfur removed by CAFB will be reduced to elemental sulfur using a modified Claus process.

An atmospheric pressure CAFB gasifier demonstration plant will be constructed and ready for integrated operation by 1977. Simultaneously with demonstration of the atmospheric pressure gasifier, a pressurized

CAFB facility will be constructed and operated in conjunction with a gas turbine. The thinking is that a pressurized CAFB can reduce costs of power generation by gas turbines by 30%.

6.2.1.7.2 Fuel pollutant characterization--As a first step in any program involving fuels, a certain minimum amount of data on fuel is necessary. Today, this must be broadened to include all potential polluting constituents. Recognizing this, EPA/CSL has issued a report on an extensive literature survey that presents data on potential pollutants (e.g., lead, cadmium, beryllium, mercury, sulfur, nitrogen, etc.) in fuels.

Since coal is to be a major energy source and existing data are inadequate for many constituents, CSL's interest is both in developing analytical techniques for trace elements and in the analyses themselves. Techniques used include neutron activation, x-ray fluorescence, atomic absorption, ion-specific electrode, direct reading optical emission and others.

Since the form of a constituent in coal may effect its pollution potential, an effort is also under way to better define the nature and composition of coal's mineral matter. These combined studies are providing information that will be helpful in determining the quantity and fate of potential pollutants in coal's use, processing or conversion to clean fuel.

6.2.1.7.3 Coal conversion

Liquid Fuels

Technology for conversion of coal to liquid fuels is being developed in the United States at an accelerated pace. This technology represents the major alternative to increased dependence on imported petroleum fuels because of present domestic demand and inability of the domestic supply to meet this demand.

Various methods are under development to produce liquid fuels from coal. Fuel products include all ranges of low-sulfur oil that can be burned directly in utility and industrial boilers, heavy oils that can be processed through a conventional refinery and naphtha. The heavier liquid fuels produced from coal retain significant (up to 2%) quantities of coal nitrogen and usually less than 1% sulfur. Control of 98+% of the inorganic coal constituents (trace metals, ash) is projected. Technologies to produce liquid fuels from coal will not be commercially available before 1980.

EPA/CSL has several activities under way to obtain data on liquid fuel from coal processes. One of these activities involves study of catalyst materials for selective removal of contaminates such as vanadium, nickel, nitrogen, sulfur and others from coal-derived oils. Such a ctalyst material must be developed to control the relatively high nitrogen content of the oil. And it must perform satisfactorily in the presence of the sulfur content of the oil.

Study of competing reactions and removal of these contaminates will increase the usefulness of these liquids (e.g., combined cycles) and result in a cleaner environment. Another data acquisition task that CSL has under way is directed toward obtaining quantification of the pollutant potential of the Solvent Refined Coal (SRC) process. Determination of material balances for sulfur and nitrogen in the SRC process was included and is currently in the process of being reported.

Work is also in progress on preparation of engineering designs of over all coal-processing complexes based on the SRC process that will produce optimally clean gaseous and liquid fuels.

A program for total environment assessment of liquid fuel from coal technologies is currently under way and is being expanded by EPA/CSL. This type of environmental assessment activity is required because of the importance of insuring that coal liquefaction technologies will include adequate environmental safeguards. Their use otherwise to meet domestic energy needs may be severely restricted because of potential environmental impact.

Liquid fuel from coal complexes of 30,000 and more tons of coal per day are projected. Obviously, technologies that treat such large quantities of coal for liquid-fuel production will also handle and process enormous quantities of sulfur, nitrogen, trace constituents and polynuclear aromatics under conditions that could lead to significant pollutant discharges without adequate process control.

This environmental assessment activity will determine those controls required for liquid fuels from coal technologies or will identify additional information that must be obtained to identify control needs. After defining process pollutant control requirements, appropriate solutions can be pursued.

Gasification

Coal conversion to a gaseous fuel is an important way to provide environmentally clean energy when done properly. A significant increase in coal gasification activity by the private sector has not taken total environmental impact into account. EPA/CSL has done studies that address this need.

Using currently available information and engineering estimates, coal conversion processes are being evaluated to determine associated environmental problems. Reports have already been issued on Koppers-Totzek, Synthane and Lurgi processes. And reports on other processes will be issued soon.

Although there are many potential problems with elements and compounds of sulfur, nitrogen, mercury, lead, cadmium, vanadium, particulates, etc., there is an urgent need for quantifying constituents in all output streams. As a result, use is being made of new environmental data obtained or planned for from existing commercial gasification complexes overseas and pilot plant operations in this country.

Through a planned and integrated effort to obtain data, do environmental assessment, identify needed environmental safeguards and research, develop and demonstrate environmental controls, energy processes that will be efficient and environmentally sound can be commercialized.

The preceding basically applies regardless of final gas Btu content. However, use of low or intermediate Btu gas presents additional problems. EPA/CSL is studying this in relation to environmental aspects of combined cycle power generation and retrofit of existing commercial and industrial facilities to use this alternate fuel source. Results to date indicate that over all gasification and power generation efficiencies will be improved with proper integration of environmental controls while developing environmentally sound systems.

These studies also help to identify alternatives and environmental needs. And some users of clean premium fuels could switch to an alternative gasified fuel with proper environmental planning and free premium fuels for premium needs.

6.2.2 Industrial Processes

6.2.2.1 Coke Making--Production of coke in conventional coke oven batteries has traditionally been a major source of particulates, sulfur oxides, odors, carcinogens and hazardous trace metals. Until recently, emissions from this source have been relatively uncontrolled.

The majority of existing coke-making facilities will be operable for the next 25 years. And most facilities built in the next 10 years are expect to feature conventional batteries. As such, CSL has studied developing control technology for conventional batteries to meet pollution control guidelines until the end of the century.

Indications are that pollution control technology developed for conventional batteries, whatever it is, will probably be expensive, have high-maintenance cost and still not control all pollutants. The expected long-term solution to the coking problem is a continuous coking process that emits pollutants in a more controllable form. CSL's involvement in coking should ultimately include continuous coke-making when it's more feasible.

Specific coke oven emission-control projects with CSL involvement includes smokeless coke charging, enclosed coking pushing and quenching, smokeless coke pushing and improved coke oven door seals.

Coke oven projects obviously concern pollutants other than hydrocarbons. Nevertheless, these projects will have a significant impact on stationary source hydrocarbon emissions.

6.2.2.1.1 Coke oven charging emission control program--EPA/CSL jointly funded an emissions control program with the American Iron and Steel Institute to improve coke oven charging techniques and abate the large volume of particulates and gases released during charging operations. The program operation was managed by Jones and Laughlin Steel Corporation at their Pittsburgh Works. The program culminated in design and construction of a new type of larry (coal charging) car that was both functional and smokeless. It also incorporated an environmentally controlled cab for safety and comfort of the operator.

The Mitre Corporation concurrently did an emissions test and evaluation program. Measurements of major gases emitted and reductions attained using the new larry car are tabulated below:

TSP (total suspended particulate)	120 gms/charge	85% reduction
THC (total hydrocarbon)	20.43 scf/charge	40% reduction
CO	6.28 scf/charge	64% reduction
CO_2	3.82 scf/charge	87% reduction
NO_x	.021 scf/charge	82% reduction

Favorable response of the coke industry to development of this improved technology is demonstrated by their commitment of $10,000,000 for new installations incorporating these and other features.

6.2.2.1.2 Enclosed coke pushing and quenching--EPA and the National Steel Corporation are funding a demonstration of an enclosed coke pushing and quenching system on National's new Weirton Steel Division Brown's Island coke plant. Construction was completed and the system placed into operation in May, 1973. The demonstration unit is presently being brought up to full production status. This will be followed by a one-year emission testing and system evaluation phase to be completed in 1975.

In this system, the coke is completely enclosed from the moment it leaves the oven until after it is quenched. Emissions produced in the push and transfer to the quench station are drawn off and removed with a high-energy scrubber on the gas cleaning car. Emissions produced by hot coke in the underground track hoppers are also controlled by a high-energy scrubber. The relatively low-volume continuous steam plume generated in the continuous quenching operation is contained by hoods and controlled by a vapor suppressor in the stack.

Current information indicates that this system will apply to nearly all new coke batteries. This is particularly significant because half of the existing coke batteries are at least 20 years old. Based on an average life of 30 years, nearly half of the 250 existing batteries will have to be replaced in the next 10 years.

Since continuous coke-making processes may not be available until the end of that period, most new batteries will be conventional slot ovens with useful lives extending well into the next century. Demonstration of this system will provide proven emission control technology that can be integrated into the initial plant design.

6.2.2.1.3 Smokeless coke pushing--CSL contracted with Ford Motor Company to test and evaluate the coke pushing emission control system developed by Koppers Company and installed at Ford's River Rouge Plant. Principal features of the system, now in operation at Ford's River Rouge Plant, Dearborn, Michigan, include a fume-collecting hood, a fume main-gas cleaning unit and a modified quench car.

Since the control system will apparently fit most, if not all, existing installations, demonstration of the Ford system will make available to industry a relatively low-cost device that can significantly reduce coke oven emissions. It will serve as an interim solution to existing batteries (more than 15 to 20 years old) until these batteries can be replaced (average battery life is 30 years). At that time, a more complete control system can be installed.

6.2.2.1.4 Coke oven door seals--Leakage of gases and condensible hydrocarbons from coke oven doors contribute significantly to typical poor air quality in the vicinity of coke batteries. These emissions contain high levels of carcinogenic materials such as benzo(a)pyrene. They are potential health hazards to workers and surrounding communities. The solution to this problem has a relatively high priority within EPA and the steel industry.

The major technical objective of this research effort is to create and develop practical solutions to sealing coke oven doors to eliminate or reduce emissions from this source to the lowest extent practical. Another objective is development of methods to measure emissions from coke oven door seals as installed on an operating commercial battery.

Work on this project is being done by Battelle Columbus Laboratories. It is co-funded by the American Iron and Steel Institute (AISI). The work was initiated in July, 1974. The primary work done to date includes problem definition, review of technology and technology transfer.

About 17 coke-producing facilities have been visited. That includes most U.S. batteries with door seal development programs or new sealing techniques being tried. New systems have been cataloged and appriased.

Arrangements have been made to conduct tests that will define the operating conditions that a door seal will encounter. These measurements include temperature, fluid pressures, warpage, material stress and composition. Other difficult sealing problems in such areas as nuclear reactor, power boilers and spacecraft are being analyzed for possible technology transfer.

6.2.2.2 Basic oxygen process (BOP) charging emission control--Primary operations to produce steel by the basic oxygen process (BOP) include charging scrap, charging hot metal, oxygen blow, chemical tests and tapping. In charging, particularly with hot metal and during oxygen blow, large quantities of emissions are produced. There is no proven technology at present to control charging emissions.

A project was initiated in June, 1973, with National Steel Corporation's Research and Development Center to develop technology for control of particulates, gases and fumes emitted in charging of basic oxygen steel-making process vessels. This development program focuses on process modifications that will allow emissions to be collected. Consideration will also be given to suppressing emissions in the vessel.

Specifications will be developed for a prototype emission-collection system. Additional specifications will be developed for a gas-cleaning system to be added to the prototype collection system. The development program is structured so that results will be applicable to the total industry.

6.2.2.3 Iron foundry--The iron foundry cupola system is the predominant U.S. process for melting and refining iron. The principal drawback of the conventional system is that effluent must be cooled by air dilution to remove particles from exhaust gases so that it can be treated by lower temperature gas-cleaning devices. This requirement produces more gas to be treated, higher gas cleaning costs and loss of heat that otherwise could be a source of non-polluting energy.

The control system that is being demonstrated to overcome the above problems involves a new water-cooled un-lined cupola coupled to a complete emission control system consisting of an afterburner, a dry media heat exchanger, a pair of cyclones and a fabric filter (the filter to be installed later). The system has been operating in the Flynn and Emrich Foundry at Baltimore.

All carbon monoxide is converted to carbon dioxide in the natural-gas-fired afterburner. The heat exchanger extracts heat from the afterburner exhaust gases, cools the gases so that they are compatible with the dust-collecting unit and does this with minimal air or water dilution. Transferring this heat to the blast air-stream reduces the amount of coke used that, in turn, reduces both coke particulate blown from the cupola and over all emissions from the coke manufacturing operation.

The dry media heat exchanger minimizes such problems as fouling of the heat transfer surfaces by contaminated cupola exhaust gases. This problem results in frequent and costly maintenance with conventional tube-type heat exchangers. The expected slight fouling of the dry media in the heat exchanger will produce only negligible performance deterioration.

Dust particles in the cooled heat exchanger exhaust-stream are removed by the cyclones and fabric filter. Since only about two-thirds of heat exchanger capacity is required for blast air heating, the remaining one-third is available as a non-polluting heat source for other foundry functions.

6.2.2.4 Sinter plant windbox emission control--The sinter plant takes ore fines, mill scale, iron-bearing particulate matter from control devices, etc. and agglomerates them into large pieces suitable for blast-furnace feed. In that way, their iron values can be recovered. This is done in a sinter machine where iron-containing material is mixed with limestone and coke breeze and fed in a thick layer on a long slow-moving continuous belt.

Coke at the top of this layer is ignited at the front end of the machine. Ambient air is drawn down through this slow-moving bed to provide oxygen for maintenance of coke combustion. The products of combustion are collected in a windbox and exhausted to the atmosphere.

As the mixture proceeds, the flame front goes deeper and deeper into the layer until it reaches the belt at the discharge end of the machine. The heat given off by the burning coke is sufficient to make other materials tacky and stick to each other. But the heat is not great enough to completely liquify it. The fused material being discharged from the machine is then broken into large pieces in a sinter breaker and screened. The screened product is used as blast-furnace feed.

The emissions contain particulates, SO_2, other gases and hydrocarbons derived from oils that are driven off by distillation on some components of the charge material.

CSL's current contract with National Steel Corporation calls for identification of windbox emissions versus feed characteristics on a conventional sinter machine and design of a windbox gas-recirculation system. The second phase, now in final stages of negotiations, calls for an extensive test and evaluation of a sinter machine fitted with a windbox gas-recirculation system.

In this approach, part of the windbox gases are returned to a hood located above the sinter bed instead of being discharged to the atmosphere. Enough ambient air is mixed with recirculated gases above the bed to provide oxygen for the process.

The recirculation approach promises several advantages, including:

1. Reduced volume of gases to be cleaned.
2. Reduced hydrocarbon emissions by using the sinter bed as an afterburner.
3. Reduced particulate emissions by using the sinter bed as a filter.

6.2.2.5 Ferro-alloy furnaces

Characterization. The Office of Air Quality Planning and Standards (OAQPS) has conducted extensive source emission tests over the past three years on a number of ferro-alloy furnaces here and abroad to establish the basis for a Standard of Performance for new ferro-alloy plants. Facilities tested included all principal ferro-alloy products along with calcium carbide that are smelted in submerged arc-furnaces

Since many of these samples still exist, CSL's program obtains these samples and results of the analysis performed by OAQPS and does more detailed and exhaustive analysis where indicated. And in those cases where there is enough sample, the samples will undergo toxicological screening tests.

This effort will result in maximum use of available samples to detect those smelting operations posing the greatest danger of hazardous element emissions. The samples would also be used for any further emission testing and R&D on improvement of control technology.

So far, samples from five different furnaces have been analyzed for 60 elements and screened for polynuclear aromatic hydrocarbons (PNA's). The elemental analyses agree well with the limited analyses performed by OAQPS.

The PNA screening that was not done previously on these samples showed high levels in some samples. The next step will be to collect new samples with recently developed procedures that guarantee preservation of the true character of samples (PNA's are susceptable to light and heat).

The submerged arc-electric furnace is the principle source of emissions in the ferro-alloy industry. Smelting of ferro-alloys is usually accomplished by reducing ore with carbon that produces desired metallics as well as substantial quantities of CO. In some cases, the quantity of CO produced actually exceeds the production of metallics. The gases evolved from ferro-alloy furnaces carry large quantities of particulates that, because of high temperatures in the reaction zone, are primarily in the submicron size range.

Conventional practice has been to leave the furnace top open. This allows the CO to mix with large volumes of air and burn above the furnace. The mixture is then collected and treated with conventional particulate control equipment before being vented to the atmosphere.

More recently, furnaces have been used in Europe and Japan that are hooded tightly so that no excess air is carried in the furnace offgas. And combustion does not take place above the furnace. When this type of system is used, the volume of gas is decreased by 20 to 50 times since excess air is not included.

This decreased amount of emissions can be cleaned to the same degree as emissions from an open furnace. So total particulates emitted are decreased by approximately the same factor of 20 to 50 times. Also, the gas that is no longer burned over the furnace can be used as a low Btu fuel after cleaning.

U.S. ferro-alloy producers hesitate to install totally enclosed furnaces because they think it may reduce their product flexibility. To solve this problem is the project goal. Specific objectives of this study include:

1. To compare flexibility of open and totally enclosed ferro-alloy furnace to learn about the true significance of the flexibility problem.

2. To identify current practices that minimize any flexibility problem that may arise in totally enclosed furnaces.

3. To develop, where warranted, recommendations for an additional program that could be undertaken by EPA to develop or demonstrate techniques and systems to minimize the problem.

6.2.2.6 Smelters--Because of substantial SO_2 emissions from non-ferrous smelters and lack of available control technology, CSL has initiated a set of development projects. Two new projects currently in operation have as their respective objectives:

a. Providing information to EPA on a smelter-by-smelter basis about optimum application of currently demonstrated technology to control all smelter streams with SO_2 and particulates at the same time.

The output will be in a form currently acceptable to the courts as demonstration by means of technology transfer.

b. The assessment of environmental considerations of emerging technology for metal-winning in the primary non-ferrous industry. In this project, consideration will be given to hydrometallurgy as new smelting processes.

CSL and Phelps Dodge Corporation started a cost-sharing study in July, 1971, of a new sulfur-oxide control method based on reacting SO_2 with H_2O and recovering the sulfur involved as elemental sulfur. Initial attempts to generate needed H_2S by roasting available copper ore with steam at 800°C showed that it was technically feasible but the economics were prohibitive.

Emphasis has now shifted to leaching the concentrate with hydrochloric acid that decomposes pyrite and pychloric in the concentrate and releases ample quantities of H_2S. Preliminary results are promising. Tests are required, however, to understand the observed variations in H_2S generation as a function of the concentrate source.

EPA has entered into two separate Public Law 480 agreements (excess foreign currency programs) with Yugoslavia. One program is with the Institute for Copper, in Bor and the other program is with the Lead and Zinc Institute, in Trepca. The Bor project is a three-year investigation (begun in May, 1971) at an American-engineered copper smelter (the largest in Europe). The Trepca project is a similar three-year effort (started in October, 1971) at a lead and zinc smelter.

Objectives of both projects are:

a. Qualitative and quantitative characterization of all air pollutant emissions from this type of smelter.

b. Relating air pollutant emissions to the feed and to feed changes so that data will apply to other smelters.

c. Relating air pollutant emissions to operations changes (changes in smelter configuration) so that data will apply to other smelters.

d. Determining the effects of controlling sulfur dioxide and particulates on emission of all other pollutants, especially "hazardous" heavy metals.

The relationships being developed in these two PL-480 projects should be applicable to the domestic non-ferrous smelting industry. Additionally, two smaller studies on potentially hazardous materials have been done.

The first was to develop methods to remove mercury from smelter gases. The results show promise.

The second was to determine the fate of various pollutants (such as As, Cd, Se, Hg and Pb) when a sulfuric acid plant is used as a SO_2 control process. Those pollutants ending up in the acid pose a potential hazard. About half of the acid manufactured domestically is used for acidulation of phosphate rock. It could be transferred to foods when used as a fertilizer.

6.2.2.7 Kraft pulping--The Pulp Mill Indirect-Contact Evaporator Conversion project at Hoerner-Waldorf Corporation is a first-of-a-kind demonstration of retro-fitting an existing furnace to eliminate the standard practice of direct contact between furnaces gases and incoming liquor. The direct contact portion of the furnace is a major source of furnace emissions.

EPA is demonstrating viability of the retrofit concept by supporting a detailed emission-testing program for both the retrofit and the new boiler. Also, capital and operating cost requirements, startup experiences and operating capabilities are being documented. And the testing program is designed to establish optimum boiler conditions for low-odor SO_2 and particulate emissions.

Preliminary indications are that a retrofitted boiler can be operated successfully. EPA's complete documentation of retrofitted furnace capability to control noxious emissions efficiently and economically will provide existing mills with a viable option for meeting local as well as anticipated Federal emissions standards.

6.2.2.8 Alfalfa dehydration--In the alfalfa industry, dehydration of harvested "raw" alfalfa is a necessary step in processing the crop to the standard final product of pelletized alfalfa. This dehydration is done in a continuous system rotary-drum dryer where gas temperatures may reach 2000°F. Because of the non-homogeneity of moisture content, however, some of the alfalfa may be so dry when introduced into the drum that it burns, producing significant particulate emissions.

The American Dehydrators Association (ADA) investigated this serious problem in 1971. EPA joined in the effort in July, 1972, by providing a grant to help the ADA further its studies. The final report on the program, finished in December, 1973, is now available.

Results of the first test phase (1971) indicate that the drying operation causes 75% of total emissions. Results of the second test phase (1972) indicate that medium-efficiency wet scrubbers have the potential to bring alfalfa dryer emissions into compliance with process weight and rate standards. Results of the third phase (1973) indicate that it is possible for each dehydrator to plan and schedule a technically and economically sound strategy to control particulate emissions so as to meet the Bay Area Process Weight Rate Standard. The report includes capital and operating costs applied to a representative control model for control schemes investigated.

6.2.2.9 Nitric acid plants--CSL is involved in a joint demonstration with the U.S. Army of the capability of molecular sieves to abate NO_x from nitric acid plants. This effort includes testing and evaluation of a molecular sieve system retrofitted to a 50-ton per day ammonia oxidation process (AOP) unit.

The objective of this program is to determine economics and operating characteristics of molecular sieves for this specific application. The program will include a thorough evaluation of the efficacy of this pollution control method. This method has the potential to allow the present NO_x performance standard for new nitric acid plants (3 pounds/ton of acid produced, expressed as NO_2) to be reduced, perhaps by as much as a factor of 10 to 20. System start-up was planned for March, 1974.

6.2.2.10 Refineries--Petroleum refinery catalytic-cracking feedstocks contain varying amounts of sulfur that are distributed between the cracked products and carbonaceous matter laid down on the catalyst during the cracking reaction. Although distribution depends on many factors, about 5% of the total sulfur generally ends up with the catalyst to be regenerated.

In 1970, estimated refinery SO_x emissions (containing 15-60% SO_3) from catalytic cracker regenerators amounted to 359,000 tons (1% of the total SO_x emitted in the U.S.). The regenerator is recognized as an important source and should be more significant as refiners process more higher sulfur crude oils.

CSL has developed a program to identify and evaluate techniques for reducing SO_x emissions from regenerators by 90%. The program will include laboratory and pilot plant studies as needed to confirm the most advantageous process identified.

6.2.2.11 Plastics and petrochemicals--The ethylene oxyhydrochlorination vent is the main source of hydrocarbon emissions associated with manufacture of ethylene dichloride, a five-billion pounds per year business. At present, there is no practical way to eliminate the oxyhydrochlorination vent from existing processes. The gases are too dilute for direct incinceration and addition of natural gas to make the gases burn is an extravagance. Furthermore, incineration will produce hydrochloric acid that must be controlled by scrubbing.

It is believed that hydrocarbon control can be done with only a modest increase in cost because anticipated benefits of increased raw material yields will off-set control costs to a great extent. Unit cost increases of 0.05¢ per pound of EDC are projected.

The objective of this 12-month project is to demonstrate technical and economic feasibility of a process to produce ethylene dichloride by ethylene oxyhydrochlorination characterized by a hydrocarbon emissions rate-reduction of 90% or greater. Current processes use air as the source of oxygen and vent the resultant inerts along with about 0.03 ton hydrocarbons per ton of EDC to the atmosphere.

The proposed process, feeding oxygen with recycle vent-gas, will be applicable to existing facilities to the extent that it will be compatible with other units of the over all process to produce vinyl chloride from ethylene and chlorine. The proposed process will probably be economically competitive with existing ethylene oxyhydrochlorination processes.

6.2.2.12 Asbestos mining--Phase I of this program involved problem definition. One asbestos-milling tailings pile and two asbestos cement-manufacturing waste piles were sampled with hi-vol samplers and the filters analyzed for asbestos. Ambient asbestos concentrations in air were evaluated using dispersion models. It was concluded that asbestos mining-and-milling waste probably did not have serious impact on public health because of remoteness of sites. It seems that asbestos cement waste probably did have high public health impact because of ambient levels calculated as present in populated areas.

A competitive procurement now in process is entitled "Field Testing of Control Concepts for Abatement of Emissions from Asbestos Manufacturing Waste." This project will involve selection of control options to reduce emissions from manufacturing waste-piles and field testing these options for technical and economic viability.

6.2.2.13 Enclosed asbestos operations--Phase I of this program involved problem definition. Five sites processing asbestos were visited and baghouses were typically 99% efficient, baghouse effluent gases contained between 10^7 and 10^9 fibers/cubic meter. It was concluded that further improvements in control efficiency may be required to protect public health.

Phase II of the program is a laboratory study to optimize baghouse performance for asbestos fibers. Various options will be tested for technical feasibility and a cost-benefit relationship established for options.

6.2.2.14 Asphalt roofing manufacturing--The primary objectives of this program are to characterize atmospheric emissions of particulate polycyclic organic matter (PPOM) from asphalt roofing manufacturing processes and to describe general demographic parameters of this industry such as size, location and growth patterns. This characterization of PPOM includes: quantitative measurements of effluent gas streams to determine concentration and emission rates of total particulate, concentrations of selected polycyclic organic compounds and particle size distribution.

Emission rates are related to various process variables to provide a basis for estimating emissions from other plants in this industry. Measurements are made before and after use of emission control systems.

Specific polycyclic compounds identified are listed below:

7,12-Dimethylbenz (a) anthracene
Dibenz (a,h) anthracene
Benzo (c) phenanthrene
3-Methylcholanthrene
Benzo (a) pyrene ($C_2 0H_{12}$)
Dibenzo (a,h) pyrene
Dibenzo (a,i) pyrene
Dibenzo (c,g) carbazole

The secondary objective of this project is to characterize other atmospheric emissions from these manufacturing processes such as aldehydes, gaseous hydrocarbons and inorganic particulate.

The following specific processes were sampled to determine emission rates:

Asphalt blowing

Felt saturating

Mineral coating

The blowing and saturating operation are, by far, the largest potential sources of PPOM. Mineral handling and coating operations are potential sources of particulate, but not PPOM. Where possible, each process was sampled while saturating felt for shingles and then roll roofing and under two operating conditions with two different asphalts.

When the PPOM and other pollutants have been characterized, a program to develop and demonstrate a control technique will be initiated if needed.

6.2.3 Particulate Control Technology

For the most part, fine particulate control is in a very early stage of development. Recently, however, actual source tests have shown that both electrostatic precipitators (ESPs) and baghouses should be capable of controlling fine particulate from a limited number of sources emitting fly ash.

An ESP has been shown to be effective on a utility boiler emitting fly ash with a resistivity conducive to electrostatic collection. On this utility boiler, burning a relatively high sulfur coal, a high efficiency ESP (99+% over all mass efficiency) was more than 90% efficient in mass removal of all particulate fractions as small as 0.02 microns.

Preliminary tests indicate that a baghouse is effective on a utility boiler if close operating limits are maintained on a number of critical variables.

It is quite possible that applicability of conventional ESPs over a broad rnage of sources to fine particulate control can be extended by developing dust-conditioning techniques and by modifying the design of charging sections and collecting electrodes. Considerable research and development will be needed before either method can be put to practice. The development of special operating techniques and filter fabrics seems to offer the best hope of extending the useful operating range of baghouses.

6.2.3.1 *Electrostatic precipitation*--In an electrostatic precipitator (ESP), dust suspended in gas streams are electrically charged and passed through an electric field where electrical forces cause particles to move toward a collection electrode. The dust, separated from the gas by being retained on the collection electrode, is later removed from the device. In a conventional ESP, the dust is removed mechanically. In a wet ESP, the dust is removed by continuous washing of the collection electrode.

A systems study of conventional ESPs has been completed. Its results are published in an ESP handbook. A systems study of wet ESPs was scheduled for completion in late 1974. A mathematical model that quantitatively describes ESP operation under all conditions and indicates potential performance limitation- and design improvements has been developed and is being up-graded to improve agreement between predicted and measured performance--especially for fine particles.

CSL is conducting field tests of industrial ESPs to determine fine-particle collection and economics of ESP systems. Recent results indicate that properly designed and operated ESPs can control fly ash from coal-fired utility boilers at over all mass efficiency in excess of 99%. These same efficiency measurements indicate that these ESPs are more than 90% efficient on a mass basis in collecting all particle size fractions as small as 0.01 microns.

A theoretically-sound method of sizing ESPs has been developed based on the mathematical model and field test results. A report describing the design method and presenting equations and figures necessary to use the method was scheduled for publication in late 1974.

ESPs are being re-designed to improve their particulate collection efficiency, especially for fine particles and high resistivity dusts. This work includes development of dust-conditioning methods and special particle-charging and collection section designs. Reports on fly ash conditioning have been published. The work on conditioning has resulted in discovery of the current carrying mechanism in fly ash at high temperatures and demonstration of a new conditioning agent.

6.2.3.2 Fabric filtration--A typical fabric filter consists of a flexible layer of porous cloth through which a dusty gas is passed to separate particles from the gas stream. Because accumulating particles increase the filter's resistance to gas flow, deposits are removed periodically by cleaning the cloth to maintain pressure drop across the filter within practical operating limits. The ability to clean the fabric without removing it is a distinguishing characteristic of this class of gas filter.

In the last year, full-scale fabric-filter systems on combustion sources have been characterized as to their ability to remove particulate as small as 0.01 μm. Test results show the filter systems to operate typically at a 99.8% over all collection efficiency and at greater than 99% efficiency even for sizes as small as 0.1 μm. Experiments have shown that fiber and fiber characteristics can be manipulated to improve filter performance. Manufacturers are producing fabrics that filter at higher efficiencies and lower pressure drops than before.

Laboratory work both in-house and by contract is continuing to determine parameters and interactions that most affect filtration performance (dust, gas, fabric, process variations and baghouse operation). Specific programs to be pursued over the next year include: development of filtration theory for needle-punched fabircs, testing of filter bags made with various special fibers, optimization of cleaning parameters, investigation and use of electrostatic phenomena, high-velocity filtration and continued characterization of existing industrial filter-systems.

6.2.3.3 Wet scrubbing--In a wet scrubber, both gaseous and particulate pollutants are transferred from the gas to a scrubbing liquid. Availability of a wide variety of scrubber types and scrubbing liquids gives wet scrubbers potential for satisfactorily removing many pollutants. (Details of many gaseous scrubbing systems are described elsewhere in this Report: See Section 6.3.1.)

Results of a wet scrubber system study have been published as a handbook. It is an authoritative and comprehensive reference source on wet scrubber technology. A system study of wet-scrubber entrainment separators is underway. The results of this study will also be published as a handbook. The first section of the handbook was scheduled for publication in late 1974.

The Control Systems Laboratory is conducting field tests of industrial wet-scrubber systems to better define fine-particle performance and economics of conventional scrubber systems. The data from these tests will also be used to improve and develop scrubber design equations.

A feasibility study of using condensation effects to improve fine-particle collection has been completed. Based on results of this study, CSL is developing a new class of scrubber systems called Flux Force/Condensation (FF/C) scrubbers for collecting fine particles. A pilot scale demonstration of FF/C scrubbers is under way.

Study of liquid and energy use in conventional scrubbers is also sponsored by CSL. Results of the first phase of this work have already been published.

6.2.3.4 Novel particulate collection devices--All known novel devices and new collection concepts are being reviewed by EPA. Those with potential for fine-particle collection are being evaluated for performance and related cost. Systems showing promise of high-efficiency fine-particle collection at reasonable cost and meriting further development will, if necessary, be further supported by CSL.

Evaluation of four novel devices has been completed. The Lone Star Steel Company Steam-Hydro scrubber installed on an open hearth furnace had 99.9% collection efficiency, the best efficiency of the devices tested. This scrubber has greatest potential where waste heat is available for steam generation since energy requirements range from 8250 to 12,750 Btu/1000 scf.

The Aeronetics two-phase scrubber has similar power requirements. Tests on an Aeronetics scrubber installed on a ferro-alloy plant gave collection efficiencies of 95.1 to 96.7%.

The RP Industries Dynactor scrubber was tested in the laboratory using re-suspended fly ash and iron oxide. It did not give high efficiency collection of submicron particulate, but in applications that a venturi scrubber might be suitable for, the Dynactor scrubber may be an economical alternative.

The Braxton Corporation sonic agglomerator was tested in the laboratory using re-suspended cupola dust and fly ash. The collection efficiency with this device was not adequate to justify further EPA development of sonic agglomeration.

Test programs are now under way to evaluate four additional novel devices, i.e., the Purity Pentapure Impinger, the Entoleter Centrifield Scrubber, the Johns-Manville CHEAF Filter and the Rexnord Granular Bed Filter. Annual evaluations of four to six devices are expected through FY 80. Laboratory pilot-scale development of one-to-three novel collection systems will be initiated in FY 75.

A feasibility study on use of charged droplets to collect fine particulate matter has been completed. Research in critical areas of charged-droplet technology, identified in the feasibility study has also been completed by M.I.T. Problems related to scale-up of the charged-droplet scrubber and eventual commercialization are to be solved under a program with TRW. Pilot demonstration of the charged droplet scrubber is scheduled for completion in 1975.

Feasibility of collection of charged particles in fiber beds has been demonstrated by Battelle Northwest. They will continue with efforts to model the collection mechanism and scale-up the device.

Other new concepts using electrostatics are being assessed. The University of Illinois is studying the electric curtain and Carnegie-Mellon University is studying electrostatic effects in fabric filtration, both under grants.

The feasibility of foam scrubbing to collect fine particles will be assessed under a contract with Monsanto Research Corporation. Demonstration of these concepts is expected in 1976.

6.3 REFERENCES

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